

# CHEMICAL ENGINEERING SCIENCE

## GENIE CHIMIQUE

VOL. 4

FEBRUARY 1955

No. 1

### Liquid-vapour equilibria in the iso-butanol—n-butanol, methanol—n-butanol and diethyl ether—n-butanol systems

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(Received 13 July, 1954)

**Summary**—Because of the paucity of data on the phase behaviour of mixtures of compounds containing active or polar groups at elevated pressure, the P-V-T-x relations of the iso-butanol-n-butanol, methanol-n-butanol and diethyl ether-n-butanol systems were determined at the liquid-vapour phase boundaries from near their atmospheric boiling points to the highest temperature and pressure at which the liquid and vapour co-exist. In addition, the vapour pressures and saturated liquid and vapour densities of the pure components were determined up to their critical points. The data are presented in the form of tables and graphs.

In so far as is indicated by the data, the phase behaviour of binary systems of the alcohols is the same as that exhibited by binary systems of hydrocarbons that belong to a given homologous series.

**Résumé**—En raison de la pauvreté des données sur les relations entre phases aux pressions élevées, pour les mélanges de composés à groupements actifs, ou polaires, les auteurs ont étudié les relations P-V-T-x pour les phases coexistantes liquide-vapeur depuis le point d'ébullition au voisinage de la pression atmosphérique jusqu'aux températures et pressions les plus élevées où les deux phases coexistent, dans les mélanges de butanol normal, avec soit l'isobutanol, soit le méthanol, enfin l'oxyde d'éthyle. En outre, on a déterminé jusqu'au point critique, les tensions de vapeur et les densités des deux phases pour les quatre constituants purs. Les résultats sont exposés sous forme de tableaux et de courbes.

Dans la limite des faits observés, le comportement des systèmes binaires d'alcools reste le même que celui des systèmes binaires d'hydrocarbures appartenant à une série homologue donnée.

The ever increasing use of high pressure in many industrial processes has greatly stimulated interest in and the need for accurate and extensive information on the liquid vapour equilibrium relations of mixtures under elevated pressures. Up to the present time, the study of these relations particularly, in the critical region, has been confined, generally, to hydrocarbon systems. Such systems, being made of up compounds of a distinctly non-polar nature, give no information on the effect of active or polar groups in the molecule on these relations. Polar groups,

as exemplified by the OH group in the alcohols and the phenols, the COOH group in the acids, the  $\text{NH}_2$  and NH groups in the primary and secondary amines and other groups, all of which contain active-H-atoms, manifest their presence in the molecule by the phenomena of association and hydration. This phenomenon, under certain circumstances due to "hydrogen bonding," materially effects the vapour-liquid composition relations in mixtures at atmospheric pressure.

The present study was undertaken for the purpose of investigating the vapour-liquid equilibrium

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relations in mixtures of polar compounds at elevated pressures. The binary systems, methanol—*n*-butanol, isobutanol—*n*-butanol and diethyl ether—*n*-butanol were selected in order to study respectively, 1) mixtures composed of compounds belonging to the same homologous series, 2) mixtures of chemical isomers and 3) mixtures of physical isomers. The P-T-x relations at the liquid-vapour phase boundaries were determined from near their atmospheric boiling points to highest temperature and pressure at which the liquid and vapour phases coexist.

HILL and VAN WINKLE [5] have determined the vapour-liquid equilibrium relations of the methanol—*n*-butanol system at 760 mm pressure. So far as is known, none of these systems of alcohols have been studied at pressures above atmospheric.

#### EXPERIMENTAL METHODS

The methods of determining the vapour pressures, the densities and the vapour-liquid equilibrium composition relations in the three binary systems, iso-butanol—*n*-butanol, methanol—*n*-butanol and diethyl ether—*n*-butanol were the same as those employed and recently described for the propane-hydrogen sulphide system [6]. These methods involved, very briefly, the determination of the P-T curves and temperature—density curves of the pure components as well as a series of mixtures of known composition in each of the above binary systems. The relations between the pressure, density, temperature and composition at the liquid and vapour phase boundaries were then derived by the construction of appropriate cross plots of these curves.

The pressure, temperature and density data for the construction of the curves were obtained by confining a small, air-free sample over mercury in a thick-walled glass tube which was surrounded by a constant temperature bath. The tube was fastened in a mercury-filled compressor block with means provided for controlling the pressure on the sample. After proper adjustment of the pressure and after equilibrium had been attained, the volume of the sample was determined by measuring the length of the column of sample, this length having been related to the volume

by a prior calibration of the tube. Since the phenomena associated with the bubble point and dew point are directly observable, the pressure, volume and temperature values for the saturated states of the sample may be obtained as exactly as the observer desires.

In the present work the temperature was measured to within 0.02°C with a copper-constantan thermocouple and a sensitive potentiometer. For the measurement of the pressure a dead weight piston gage similar to that previously described [6] was used. Its sensitivity was 0.02 pound per square inch. The experimental tube was constructed of precision bore capillary whose volume per millimetre of length amounted to 0.00320 cc (approximately 2.0 mm bore). A cathetometer, reading to 0.05 mm, was used to measure the length of the tube occupied by the sample. The methods of calibrating the thermocouple, pressure gauge and tube have been adequately described [6].

#### MATERIALS

High purity commercial samples of methanol, *n*-butanol and isobutanol were used as the starting material for the preparation of the pure liquid compounds that were studied. Purification was effected by distillation in the presence of a desiccating agent since the butanols form azeotropes with water. For this purpose bright magnesium turnings were used with the butanols and metallic sodium with methanol.

The distillation equipment consisted of a silvered and vacuum-jacketed column, 25 mm in diameter and 2 metres high, filled with glass helices of 3 mm, inside diameter and attached by a ground joint to a 2-litre boiling flask. The still head was provided with a reflux control device so that the reflux ratio could be set and accurately measured. All distillations were carried out with a reflux ratio of 19 : 1 or higher. The receiver in which the distillate was caught was attached by a ground joint to the head and was equipped with a vent and with a stopcock at the bottom for withdrawing the product. A drying tube containing phosphorous pentoxide dispersed on glass wool was attached to the vent

to prevent absorption of moisture from the surrounding air.

Approximately 1500 ml of liquid and 15 grams of desiccating agent were charged to the still and a middle fraction of about 200 ml was taken as the purified sample.

Diethyl ether of "analytical reagent" grade was used without any additional purification except that associated with the degassing operating which will be described later.

Prior to their use, a sample of each of the purified liquids was tested for contamination by measuring, in the experimental apparatus, the difference between the bubble and dew point pressures at some elevated temperature. The standard boiling point, the density at 0°C and the critical temperature, pressure and density were also determined and compared with reliable published values of these properties. The results are summarized in Table I.

#### DEGASSING AND PREPARATION OF MIXTURES

Air and other non-condensable gases were removed from the liquid samples by a series of operations which involved freezing with liquid nitrogen and pumping off the residual gas over the solid, followed by melting and distillation at low pressure. Fig. 1 is a diagrammatic sketch of the apparatus for the degassing operation as well as for the preparation of mixtures of known composition in the experimental tube.

Fifty millilitres of pure liquid were charged to bulb 4 and the bulb was attached to the vacuum

line by means of a mercury-sealed ground joint. Stopcock 3 was opened, momentarily, in order to remove most of the air-rich vapour over the liquid, before freezing the sample. As soon as the sample was frozen, stopcock 3 was opened and the space over the solid evacuated until the pressure was less than  $1 \times 10^{-5}$  mm Hg. Cock 3 was then closed and the sample allowed to melt, after which 3 was opened, cautiously, and vapour pumped off again. This procedure was repeated 3 times. Next, the cooling flask was brought up around 2, and cocks 5, 7, 9 and 17 were closed, cocks 1 and 3 opened, and the liquid in 4 was distilled and collected in bulb 2, except for a small residue which was pumped off into the cold trap 18. After evacuating the space over the solid, cock 1 was closed, the solid melted and a small fraction of the vapour pumped off. Cock 17 was then closed, 3 opened and the sample was distilled and collected in 4, except for a small residue which was discarded as before. The distillation, back and forth between 4 and 2, was repeated three times. The pure degassed sample was then stored in bulb 2 in the solid state until ready to use. The second liquid component was treated in like manner and stored in bulb 6.

The experimental tube, 16, was attached to the vacuum line by a mercury-sealed ground joint, 15, as shown in the sketch. 14 was a small hair-size capillary which extended into the tube to within 8 cm of the end. The capillary was drawn from the tube of the female half of the ground joint, 13. No lubricant was used on this joint. Communicating with the capillary through side tube, 10, was a mercury reservoir. Mercury from the reservoir could be transferred to the experimental tube by adjustment of the pressure over the mercury in the reservoir.

In the preparation of a mixture of known composition a quantity of liquid was transferred by distillation from the storage bulb to the small capillary, 8, (0.65 mm bore) whose volume per unit length had been previously determined. From the length of the tube occupied by the sample at 0°C (measured with a cathetometer reading to 0.05 mm) and the density of the liquid at 0°C, the weight of the sample was calculated. A correction was made for the weight of the

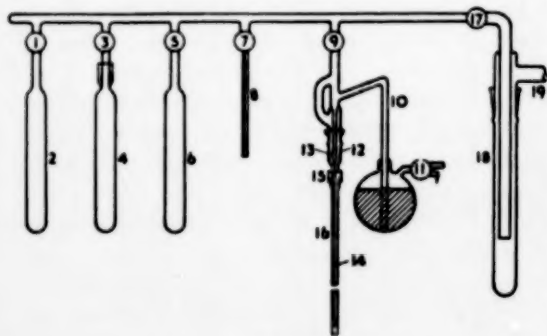


Fig. 1. Apparatus for degassing and preparing mixtures of liquid samples.

vapour over the liquid, using the perfect gas law and a knowledge of the vapour pressure and the total volume of 8 up to cock 7.

Before transferring the measured sample to the experimental tube, the tube was flushed several times with a small amount of sample which was then discarded to trap 18. By chilling the tip of the experimental tube and by manipulation of the appropriate stopcocks the liquid was distilled into 16. In like manner a measured quantity of the second liquid was transferred to 16. The sample was then allowed to melt and fill the end of the tube, after which it was frozen again. Mercury was admitted from the flask by admitting air through cock 11. The mercury entered the tube through the hair capillary just above the frozen sample and rose in the tube until the tube was completely filled. In this manner any trace of residual gas in the tube was displaced by the mercury.

Cock 9 was closed and the tube and adapter 12, lowered from the apparatus. Joint 13 was disconnected and capillary 14 removed from the tube. The tube was then transferred to the compressor block and fastened in place, as has been described [6].

#### EQUILIBRIUM DATA

The P-V-T relations at the saturated states of the four pure substances and of a total of eleven mixtures of known composition of the binary systems, iso-butanol-n-butanol, methanol-

n-butanol, diethyl ether-n-butanol, were determined. Figs. 2 to 9 are plots of the experimental data. The critical temperature and critical pressure of the pure compounds and the mixtures were observed directly, whereas the pressure, temperature and density at the maximum pressure point and the maximum temperature point on the P-T border curves as well as the critical density of the mixtures, were read from large scale plots of the data. Critical densities of the pure compounds were obtained by the application

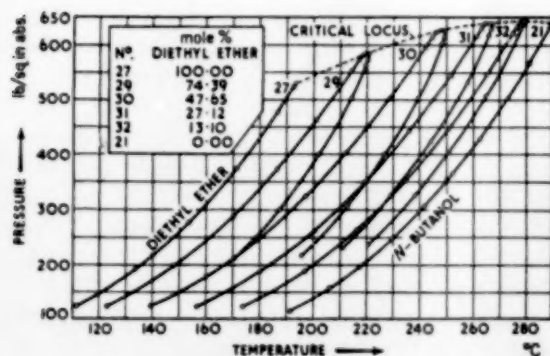


Fig. 2. P-T border curves of the ethyl ether-n-butanol system.

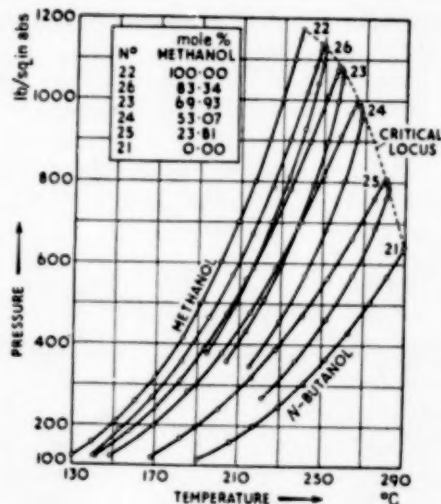


Fig. 3. P-T border curves of the methanol-n-butanol system.

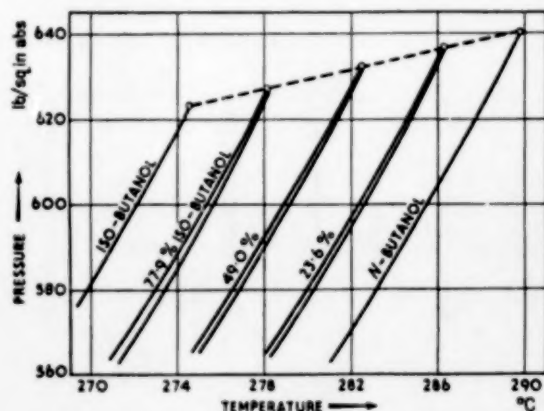


Fig. 4. P-T border curves of the iso-butanol-n-butanol system.



of the law of rectilinear diameters. The critical data for the pure substances and for the mixtures are given respectively, in Tables I and II and,

where possible, are compared with values reported in the literature. Figs. 8 and 9 show graphically the relation between the composition and the

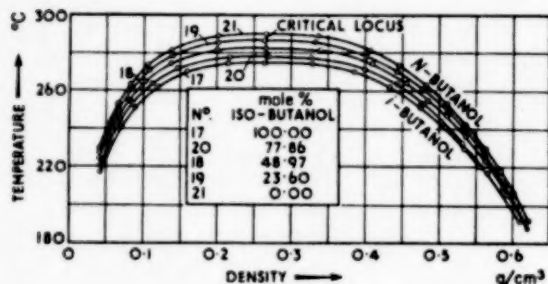


Fig. 5. Temperature-density relations in the iso-butanol-n-butanol system.

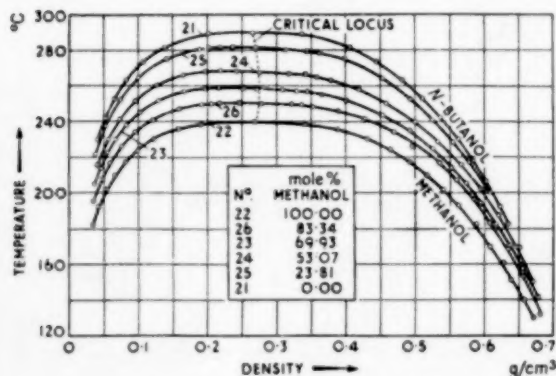


Fig. 6. Temperature-density relations in the methanol-n-butanol system.

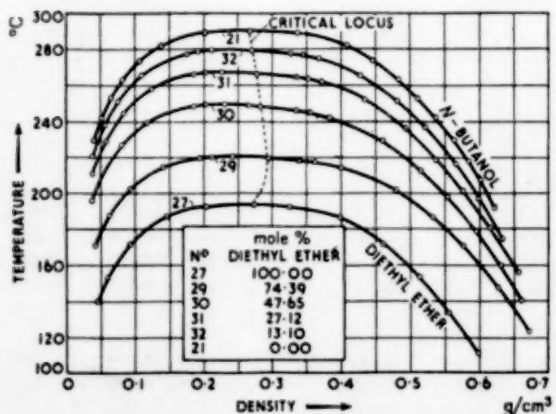


Fig. 7. Temperature-density relations in the ethyl ether-n-butanol system.

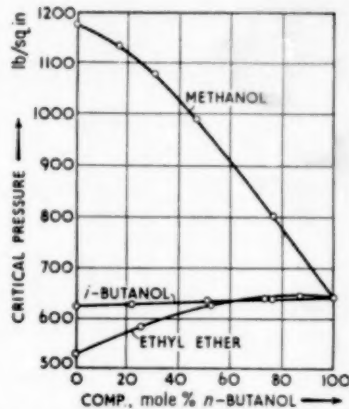


Fig. 8. Critical pressure-composition relations in binary systems of n-butanol with iso-butanol, methanol and ethyl ether.

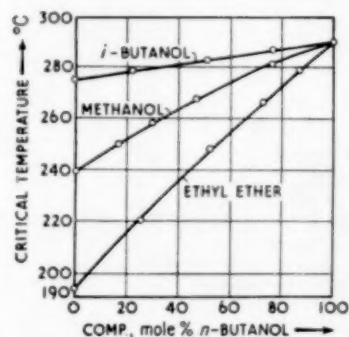


Fig. 9. Critical Temperature-composition relations in binary systems of n-butanol with iso-butanol, Methanol and ethyl ether.

critical pressure and the critical temperature for each of the binary systems. Table III and IV (a), (b) and (c) summarize, respectively, the saturated properties of the pure compounds and the various mixtures at uniform intervals of temperature. In Table III selected literature values for some of the compounds are included.

The tables were constructed from the experimental data by a combination of analytical and graphical procedures. The relation between pressure and temperature was formulated by

Table I. Physical properties of materials studied.

	<i>i</i> -Butanol	Methanol	Ethyl ether	<i>n</i> -Butanol
<b>Standard boiling point, °C</b>				
Experimental	107.83	64.55	34.47	117.73
TIMMERMANS [9]	107.89 — 108.10	64.50 — 64.75	34.40 — 34.60	117.7 — 118.0
<b>Density at 0°C, g/cc</b>				
Experimental	0.8175	0.8100	0.7363	0.8245
TIMMERMANS [9]	0.8170 0.8171	0.8100 — 0.8101	0.7362 — 0.7363	0.8246 — 0.8247
<b>Pressure rise on condensation</b>				
At vapour pressure, lb./in. <sup>2</sup>	0.87	0.49	0.94	0.32
At temperature, °C	305.7 229.48	412.6 182.34	277.0 153.72	246.7 229.70
<b>Critical pressure, lb./in.<sup>2</sup></b>				
Experimental	622.8	1174.4	529.6	640.4
Literature		1153.6 [9] [10]	523.25 [9] [10] 530.52 [7]	711.11 [9] [4]
<b>Critical temperature, °C</b>				
Experimental	274.59	239.43	193.41	289.74
Literature	279.07 [9] [1]	240. [10] [9] 240.2 [9] [2]	193.8 [9] [10] 193.9 [9] [7] [8]	287.0 [9] [4]
<b>Critical density, g/cc</b>				
Experimental	0.269	0.272	0.265	0.267
Literature		0.275 [9] [2]		

Table II. Composition and critical constants of mixtures of *n*-butanol

Composition % <i>i</i> -Butanol	Critical point			Maximum temperature point			Maximum pressure point		
	Temp. °C	P lb./in. <sup>2</sup>	Density g/cc	Temp. °C	P lb./in. <sup>2</sup>	Density g/cc	Temp. °C	P lb./in. <sup>2</sup>	Density g/cc
77.86	278.11	626.9	0.269						
48.97	282.48	632.2	0.268						
23.60	286.25	636.6	0.268						
<b>Mol % MeOH</b>									
83.84	249.84	1133.1	0.275	250.25	1127.6	0.238	249.40	1135.1	0.315
69.93	258.22	1077.5	0.276	258.89	1065.6	0.225	257.55	1082.0	0.322
53.07	267.27	988.1	0.275	268.27	969.4	0.218	266.40	996.5	0.324
23.81	280.96	798.9	0.271	281.58	785.6	0.222	279.94	806.9	0.315
<b>Mol % ether</b>									
74.39	219.49	582.8	0.293	220.86	581.8	0.238	220.38	584.0	0.259
47.65	247.94	625.3	0.284	249.59	622.1	0.224	248.76	625.9	0.254
27.12	266.04	639.5	0.277	267.41	637.9	0.221	266.78	639.9	0.252
13.10	278.57	642.4	0.272	279.25	641.1	0.228	279.20	642.5	0.251

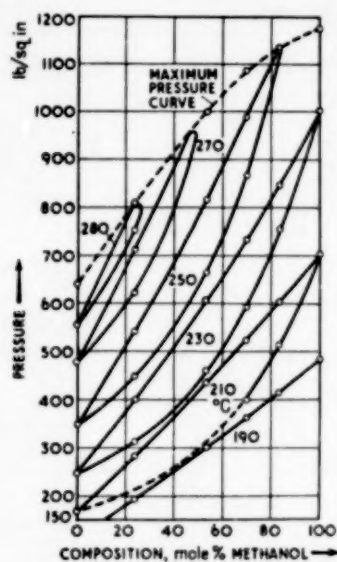


Fig. 10. Pressure-composition relations. Methanol-n-butanol system.

fitting an equation of the form  $\log P = A - B/T$  to the vapour pressure data for the pure compounds and to the dew and bubble points for each composition investigated; points in the retrograde region were excluded. The equations thus obtained (two for each mixture) were used to calculate the saturation pressures for each

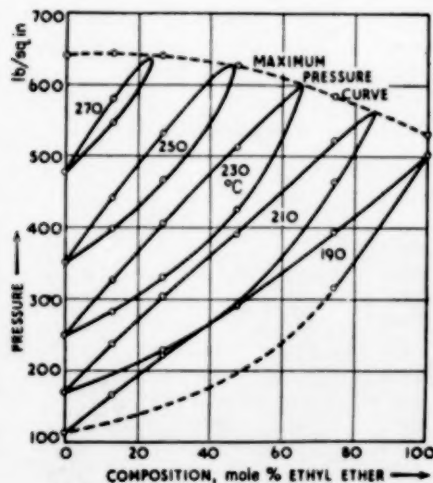


Fig. 11. Pressure-composition relations. Ethyl ether-n-butanol.

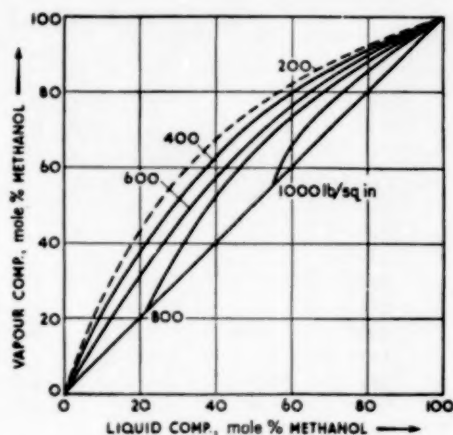


Fig. 12. Y-X diagram for methanol-n-butanol system.

experimental temperature. The calculated pressures were then compared with the measured values and graphical residual functions were constructed. These residuals could be plotted very precisely, since the maximum difference between the experimental pressure and that calculated from the appropriate equation never exceeded 35 pounds per square inch for any mixture. The scatter of the residuals about a smooth curve seldom exceeded 0.3 pounds per square inch and serve as an indication of the consistency of the data.

The densities given in Tables III and IV were read from large scale plots of the curves shown in Figs. 5, 6 and 7.

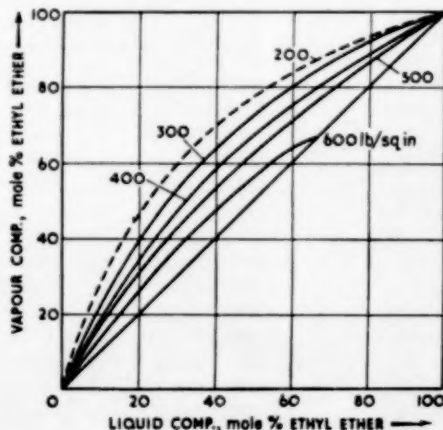


Fig. 13. Y-X diagram for ethyl ether-n-butanol system.

Table III. Vapour pressure and orthobaric densities of pure components.  
Diethyl Ether

Temp. °C	Pressure lb./in. <sup>2</sup>		Density g/cc			
	Exp.	Ref. [9] [10]	Liquid		Vapour	
			Exp.	Ref. [9] [10]	Exp.	Ref. [9] [10]
110	118.9	117.61	·5996	·5942		
120	146.7	145.28	·5822	·5764		
130	179.1	177.03	·5633	·5580		
140	216.5	213.69	·5435	·5385	·0449	·04488
150	259.5	256.44	·5210	·5179	·0561	·05551
160	308.8	305.10	·4954	·4947	·0702	·06911
170	365.0	361.04	·4657	·4658	·0886	·08731
180	428.9	421.06	·4304	·4268	·1147	·1135
190	501.2	493.34	·3687	·3663	·1690	·1620
C 193.41	529.6		·265		·265	

## Methanol

Temp. °C	Pressure lb./in. <sup>2</sup>		Density g/cc			
	Exp.	Ref. [9] [10]	Liquid		Vapour	
			Exp.	Ref. [9] [10]	Exp.	Ref. [9] [10]
130	121.5	120.70	·6718	·6770		
140	157.8	156.07	·6574	·6640		
150	201.9	199.86	·6420	·6495		
160	255.0	251.90	·6208	·6340		
170	318.3	315.04	·6081	·6160		
180	393.2	388.46	·5891	·5980	·0332	·03186
190	481.4	475.98	·5681	·5770	·0412	·04010
200	583.8	575.99	·5448	·5530	·0523	·05075
210	702.7	691.68	·5170	·5255	·0670	·06521
220	840.8	823.22	·4811	·4900	·0896	·08635
230	1000.4	974.85	·4321	·4410	·1230	·1187
C 239.43	1174.4		·272		·272	

## n-Butanol

Temp. °C	Pressure lb./in. <sup>2</sup>	Density g/cc	
		Liquid	Vapour
190	112.2	·6251	
200	138.9	·6109	
210	170.2	·5956	
220	206.6	·5759	
230	248.1	·5618	·0417
240	295.4	·5422	·0507
250	349.0	·5197	·0625
260	409.2	·4917	·0778
270	477.5	·4585	·0987
280	544.4	·4146	·1317
C 289.74	640.4	·267	·267



Table III. (cont.)  
iso-Butanol

Temp. °C	Pressure lb./in. <sup>2</sup>	Density g/cc	
		Liquid	Vapour
220	258.8	.5555	.0453
230	308.4	.5338	.0561
240	364.5	.5032	.0700
250	427.9	.4789	.0880
260	500.1	.4412	.1143
270	582.2	.2830	.1614
C 274.59	622.8	.269	.269

C = critical point.

Table IV. Summary of pressure, temperature and density data at phase boundaries.  
(a) iso-Butanol—n-Butanol Systems

Composition % i-Butanol	Temp. °C	Saturated P lb./in. <sup>2</sup>	Liquid density g/cc	Saturated P lb./in. <sup>2</sup>	Vapour density g/cc
77.86	200	169.0	.5963		
	210	205.2	.5795		
	220	246.8	.5609	244.2	.0418
	230	294.1	.5403	291.6	.0513
	240	347.8	.5167	345.4	.0638
	250	408.5	.4885	406.3	.0796
	260	477.5	.4549	475.4	.1022
	270	555.6	.4096	553.5	.1389
	C 278.11	626.9	.269	626.9	.269
48.97	190	128.6	.6158		
	200	158.4	.6008		
	210	192.8	.5853		
	220	232.2	.5678		
	230	277.2	.5485	273.9	.0472
	240	328.3	.5261	325.2	.0585
	250	386.4	.5004	383.6	.0731
	260	452.2	.4703	449.9	.0924
	270	526.1	.4307	524.6	.1205
	280	609.5	.3600	608.8	.1825
	C 282.48	632.2	.268	632.2	.268
23.60	200	148.1	.6054		
	210	180.9	.5898		
	220	218.7	.5781		
	230	262.0	.5550	259.8	.0438
	240	310.9	.5347	308.7	.0541
	250	366.5	.5100	364.4	.0671
	260	429.7	.4803	427.5	.0841
	270	500.8	.4442	498.6	.1079
	280	580.9	.3910	578.6	.1434
	C 286.25	636.6	.268	636.6	.268

C = critical point.

Table IV-b (cont.)  
(b) Methanol-n-Butanol System

Composition mol % MeOH	Temp. °C	Saturated P lb./in. <sup>2</sup>	Liquid density g/cc	Saturated P lb./in. <sup>2</sup>	Vapour density g/cc
53.07	150	126.3	-6713		
	160	159.5	-6589		
	170	198.8	-6458		
	180	245.0	-6312		
	190	299.0	-6157		
	200	361.2	-5983		
	210	432.4	-5789		
	220	513.4	-5562	377.5	-0451
	230	604.7	-5300	456.6	-0570
	240	704.7	-4992	550.3	-0720
	250	814.5	-4600	662.5	-0923
	260	932.0	-4048	796.2	-1258
	MP 266.4	996.5	-324		
	C 267.27	988.1	-275	988.1	-275
	MT 268.3			969.4	-218
23.81	170	126.4	-6514		
	180	157.3	-6378		
	190	193.3	-6232		
	200	235.0	-6077		
	210	282.8	-5903		
	220	337.3	-5715		
	230	398.8	-5504	312.4	-0451
	240	466.5	-5273	374.4	-0563
	250	540.7	-5011	446.0	-0708
	260	623.1	-4695	528.6	-0897
	270	713.9	-4272	623.8	-1188
	MP 279.9	806.9	-315		
	C 280.96	798.6	-271	798.6	-271
	MT 281.6			785.6	-222
83.34	140	136.6	-6735		
	150	174.3	-6601		
	160	219.9	-6459		
	170	274.3	-6303		
	180	338.5	-6138		
	190	413.6	-5957		
	200	500.5	-5751	416.9	-0397
	210	600.6	-5517	511.2	-0510
	220	715.2	-5230	622.6	-0652
	230	844.9	-4882	753.7	-0855
	240	989.0	-4393	908.6	-1169
	MP 249.4	1135.1	-315		
	C 249.84	1133.1	-275	1133.1	-275
	MT 250.3			1127.6	-238

MP = Maximum Pressure Point.

MT = Maximum Temperature Point.

C = Critical Point.

VOL.  
4  
1955

Liquid-vapour equilibria in the iso-butanol—n-butanol, methanol—n-butanol and diethyl ether—n-butanol systems

(b) *Methanol—n-Butanol System*

Composition mol % MeOH	Temp. °C	Saturated P lb./in. <sup>2</sup>	Liquid density g/cc	Saturated P lb./in. <sup>2</sup>	Vapour density g/cc
69.93	150	152.0	·6664		
	160	191.9	·6525		
	170	239.3	·6372		
	180	295.0	·6210		
	190	360.2	·6030		
	200	435.7	·5831		
	210	522.2	·5611	398.8	·0413
	220	620.2	·5367	486.9	·0527
	230	730.1	·5078	591.3	·0673
	240	852.7	·4698	714.4	·0876
	250	985.6	·4154	864.9	·1213
	MP 257.6	1082.0	·322		
	C 258.22	1077.5	·276	1077.51	·276
	MT 258.9			1065.6	·225

Table IV-c (cont.)

(c) *Ethyl Ether—n-Butanol System*

74.39	130	141.7	·6569		
	140	171.1	·6393		
	150	204.9	·6209		
	160	243.5	·6006		
	170	287.2	·5782	209.5	·0419
	180	336.6	·5528	258.1	·0529
	190	391.8	·5214	315.5	·0673
	200	453.1	·4849	383.1	·0878
	210	520.9	·4340	463.0	·1194
	C 219.49	582.8	·2930	582.8	·293
	MP 220.4			584.0	·259
	MT 220.9			581.8	·238
47.65	140	125.0	·6616		
	150	149.8	·6460		
	160	178.5	·6298		
	170	211.2	·6122		
	180	247.6	·5933		
	190	289.9	·5727		
	200	336.7	·5491	237.2	·0419
	210	389.2	·5220	289.7	·0531
	220	447.1	·4908	351.3	·0677
	230	510.6	·4530	423.2	·0886
	240	579.9	·3992	507.4	·1201
	C 247.94	625.3	·284	625.3	·284
	MP 248.8			625.9	·254
	MT 249.6			622.1	·224

MP = Maximum Pressure Point.

MT = Maximum Temperature Point.

C = Critical Point.

Table IV-c (cont.)  
(c) Ethyl Ether—*n*-Butanol System

Composition mol % Ether	Temp. °C	Saturated P lb./in. <sup>2</sup>	Liquid density g/cc	Saturated P lb./in. <sup>2</sup>	Vapour density g/vv
27.12	160	131.1	-6487		
	170	157.0	-6327		
	180	186.7	-6162		
	190	220.7	-5983		
	200	259.1	-5791		
	210	302.6	-5580	227.2	-0398
	220	351.3	-5354	274.8	-0480
	230	405.5	-5101	329.9	-0602
	240	465.4	-4802	393.3	-0762
	250	531.4	-4431	466.4	-0986
	260	603.6	-3873	552.6	-1340
	C 266.04	639.5	-277	639.5	-277
	MP 266.8			639.9	-252
	MT 267.4			637.9	-221
13.10	180	138.5	-6259		
	190	166.6	-6102		
	200	199.1	-5942		
	210	236.2	-5771		
	220	278.4	-5587	233.8	-0388
	230	326.1	-5379	280.9	-0471
	240	379.8	-5132	335.0	-0588
	250	439.8	-4834	396.7	-0746
	260	506.5	-4489	467.1	-0953
	270	580.3	-4014	547.0	-1273
	C 278.58	642.4	-272	642.4	-272
	MP 279.2			642.5	-251
	MT 279.3			641.1	-228

MP = Maximum Pressure Point.

MT = Maximum Temperature Point.

C = Critical Point.

Figs. 10 and 11 are constant temperature plots of the relation between pressure and composition at the bubble and dew points of the methanol—*n*-butanol and diethyl ether—*n*-butanol systems.

Table V (a), (b) and (c) presents the liquid-vapour composition data for the three systems, in terms of the familiar  $y$ ,  $x$  and  $K$  ( $K = y/x$ ) parameters. Figs. 12, 13, 14 and 15 show some of these data graphically. The table was constructed from values read directly from large scale plots of temperature-composition isobars.

In general, only the last significant figure of

any value appearing in the tables is subject to uncertainty. The pressure and temperature values are estimated to be accurate to within  $\pm 0.5$  pounds per square inch and  $\pm 0.05^\circ\text{C}$ , respectively. The uncertainty in the density values is somewhere between 0.0020 gram per cc for the liquid and 0.00020 gram per cc for the vapour, though some of the recorded values in the critical region of the mixtures may be subject to an error as large as 0.006 gram per cc. The compositions given for the mixtures are accurate to within 0.05 mole per cent.



Table V. Temperature-composition relation at constant pressure.

P lb./in. <sup>2</sup>	Temp. °C	x	y	K <sub>i-BuOH</sub>	K <sub>n-BuOH</sub>
400	245.75	100.0	100.0	1.00	
	247	90.2	91.7	1.02	-847
	249	74.6	77.6	1.04	-882
	251	58.7	62.6	1.07	-906
	253	43.1	46.8	1.09	-935
	255	27.4	30.2	1.10	-961
	257	11.8	13.2	1.12	-984
	258.5	0.0	0.0		1.00
600	272.03	100.0	100.0	1.00	
	274	85.2	86.4	1.01	-919
	276	70.3	72.3	1.03	-933
	278	55.4	57.9	1.05	-944
	280	40.5	42.9	1.06	-960
	282	25.7	27.3	1.06	-978
	284	10.7	11.3	1.06	-993
	285.4	0.0	0.0		1.00

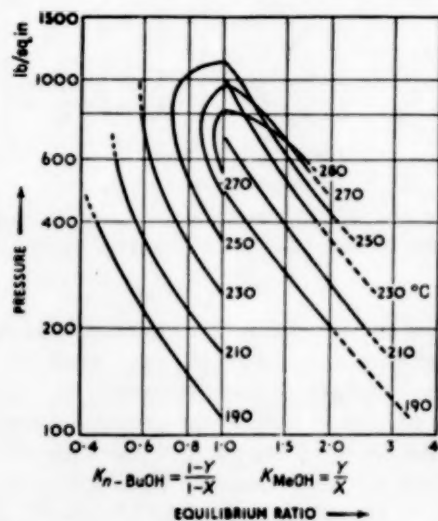


Fig. 14. Pressure-equilibrium ratio curves at constant temperature. Methanol-n-butanol system.

## DISCUSSION

The combination of the vapour pressure curves of the pure components and the P-T border curves of the mixtures form a space diagram representing the P-T-x relations of the system.

Table V  
(c) Ethyl Ether-n-Butanol System

P lb./in. <sup>2</sup>	Temp. °C	x	y	K <sub>Ether</sub>	K <sub>n-BuOH</sub>
200	135.8	100.0	100.0	1.00	
	140	90.6	97.0	1.07	-319
	150	71.9	90.0	1.25	-356
	160	56.4	81.8	1.45	-417
	170	43.2	72.4	1.68	-486
	180	31.5	61.5	1.95	-562
	190	21.6	48.9	2.26	-652
	200	12.9	34.3	2.66	-754
	210	5.3	16.8	3.17	-879
	218.3	0.0	0.0		1.00
300	158.3	100.0	100.0	1.00	
	160	96.2	98.7	1.03	-342
	170	77.8	91.0	1.17	-405
	180	63.0	82.2	1.30	-481
	190	49.8	72.3	1.45	-552
	200	37.7	61.3	1.63	-621
	210	26.8	48.9	1.82	-698
	220	17.1	34.7	2.03	-788
	230	8.3	18.9	2.28	-884
	240.9	0.0	0.0		1.00
400	175.7	100.0	100.0	1.00	
	180	92.4	96.1	1.04	-513
	190	76.8	86.7	1.13	-566
	200	62.3	77.0	1.24	-610
	210	49.2	66.6	1.35	-657
	220	37.2	55.3	1.49	-712
	230	26.2	42.8	1.63	-775
	240	16.2	28.7	1.77	-851
	250	7.0	13.7	1.96	-928
	258.6	0.0	0.0		1.00
500	189.8	100.0	100.0	1.00	
	200	84.9	90.0	1.06	-662
	210	70.7	79.8	1.13	-689
	220	57.4	69.2	1.21	-726
	230	45.0	58.0	1.29	-764
	240	33.3	46.1	1.38	-808
	250	22.2	33.5	1.51	-858
	260	12.0	19.8	1.65	-911
	270	2.6	4.8	1.85	-977
	273.1	0.0	0.0		1.00
600	230.0	65.1	65.1	1.00	1.00
	240	50.9	56.8	1.12	-880
	250	38.2	45.4	1.19	-883
	260	26.6	33.5	1.26	-906
	270	15.8	21.0	1.33	-938
	280	5.3	7.5	1.42	-977
	285.4	0.0	0.0		1.00

Table V  
(b) Methanol—*n*-Butanol System

<i>P</i> lb./in. <sup>2</sup>	Temp. °C	<i>x</i>	<i>y</i>	<i>K</i> <sub>MeOH</sub>	<i>K</i> <sub>n-BuOH</sub>
200	149.6	100.0	100.0	1.00	
	160	73.6	89.1	1.21	.412
	170	53.6	77.9	1.45	.476
	180	38.0	65.7	1.73	.553
	190	25.7	52.2	2.03	.643
	200	15.7	36.1	2.30	.758
	210	6.9	17.2	2.49	.871
	215	2.7	6.9	2.56	.956
	218.3	0.0	0.0		1.00
400	180.8	100.0	100.0	1.00	
	190	80.0	91.2	1.14	.440
	200	62.0	81.2	1.31	.495
	210	47.5	70.0	1.47	.571
	220	35.2	57.7	1.64	.653
	230	24.2	44.0	1.82	.739
	240	14.8	29.2	1.97	.831
	250	6.6	13.8	2.09	.923
	255	2.7	5.8	2.15	.968
	258.6	0.0	0.0		1.00
600	201.4	100.0	100.0	1.00	
	210	83.6	91.8	1.10	.500
	220	66.7	81.6	1.22	.553
	230	52.6	70.4	1.34	.624
	240	40.9	58.8	1.44	.697
	250	30.5	46.5	1.52	.770
	260	21.1	33.8	1.60	.839
	270	12.6	20.7	1.64	.907
	280	4.2	7.5	1.71	.970
	285.41	0.0	0.0		1.00
800	217.2	100.0	100.0	1.00	
	220	94.9	97.3	1.03	.529
	230	78.0	87.0	1.12	.591
	240	63.7	76.3	1.20	.653
	250	51.3	65.3	1.27	.713
	260	40.9	53.7	1.31	.783
	270	31.4	40.1	1.28	.873
	280	22.9	25.1	1.10	.971
	282.3	21.4	21.4	1.00	1.00
1000	230.0	100.0	100.0	1.00	
	240	84.3	89.1	1.06	.694
	250	71.0	77.9	1.10	.762
	260	59.8	65.7	1.10	.853
	267.7	54.0	54.0	1.00	1.00

These diagrams for the diethyl ether—*n*-butanol, methanol—*n*-butanol and iso-butanol—*n*-butanol

systems are shown in Figs. 2, 3 and 4 respectively. The broken line in each of the diagrams is the critical locus or envelope curve defining the critical state for all mixtures of the components. The shape of the critical locus appears to be a function, principally, of the relative volatility of the two pure components so long as they do not form an azeotrope. If it be assumed that the critical temperature of any mixture is the mole fraction average of the critical temperatures of the components, then, on the assumption that the critical pressure of the mixture is the sum of the partial pressures of the components at the critical

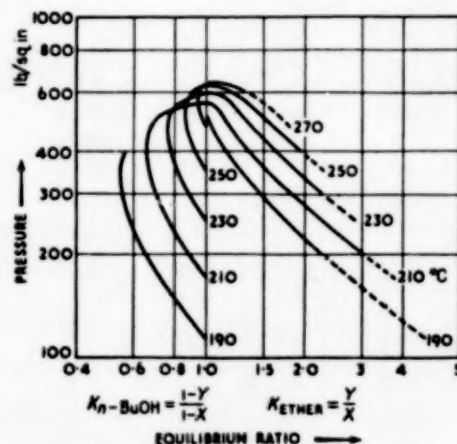


Fig. 15. Pressure-equilibrium ratio curves at constant temperature. Ethyl ether—*n*-butanol system.

temperature, the shape of the critical locus curve can be predicted, qualitatively. Thus, if the relative volatility of the components is close to unity, that is, if the vapour pressure curves lie close together and are parallel, and their critical pressures are about the same, the critical locus would be predicted to be a straight line. These conditions are fulfilled and the prediction amply verified by the results on systems composed of chemical isomers such as the iso-butanol—*n*-butanol system, Fig. 4. If the vapour pressure curves of the components are not too widely separated and the component having the lower critical temperature has the higher critical pressure, then the critical locus will be convex

upwards as in the case of the methanol-n-butanol system, Fig. 3. If the relative volatility of the components were greater, the locus would be expected to contain a point of maximum pressure. A similar result would be expected if the component having the greater critical temperature has the greater critical pressure. In both cases there must be a minimum value of the relative volatility at which the maximum pressure point just appears. The diethyl ether-n-butanol system illustrates such a case, since the point of maximum pressure is only 2.5 pounds per square inch higher than the critical pressure of n-butanol.

The critical loci of the three binary systems were calculated in the manner indicated, the "vapor pressures" of iso-butanol, methanol and diethyl ether, above their critical temperatures being estimated by extrapolating the vapor pressure curve plotted as the logarithm of the pressure versus the reciprocal of the absolute temperature. The calculated curves were found to be in surprisingly good agreement with the experimental curves considering the approximate nature of the assumptions. The maximum deviation in the critical pressure amounted to approximately 5% for the diethyl ether-n-butanol and methanol-n-butanol systems and to about 1% in the case of the iso-butanol-n-butanol system. This method of calculation, however, is not one of general application. In hydrocarbon systems, for example, the deviations between calculated and experimental critical pressures may be very large.

Information on the magnitude of the deviation of the three systems from ideal behaviour is given by a comparison of the vapour-liquid equilibrium ratio,  $K = y/x$ , for n-butanol in each of the systems, with the value calculated [8] from ideal solution laws using the fugacities instead of vapour pressures. The data are presented in Fig. 16 as curves of  $\log P$  versus  $\log K$ . As will be noted, at the lower pressures all of the curves lie very close together indicating an approach to ideal behaviour. At higher pressures, however, the nature of the associated component exerts a major influence and the experimental curves pass through a minimum  $K$  value and terminate at a pressure where  $K = 1$ ,

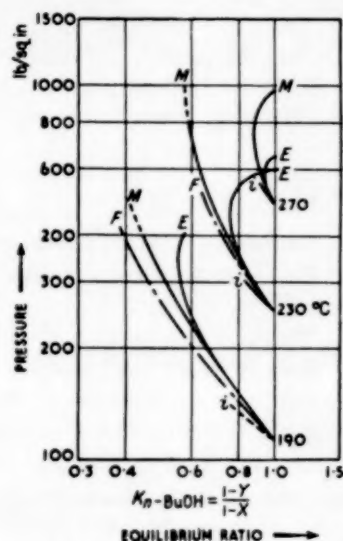


Fig. 16. Comparison of equilibrium ratio curves for n-butanol in different liquids: i—iso-butanol, M—methanol, E—ethyl ether, F—ideal solution.

which is the critical pressure for a specific mixture of the two components. At the critical point, all mixtures deviate from ideal solutions in their behaviour. In the systems concerned, n-butanol shows the least deviation in mixtures with iso-butanol and the greatest deviation in mixtures with ethyl ether.

The difference between the values of the vapour pressure and saturated densities for methanol and diethyl ether, and those selected from the literature by TIMMERMAN [10] as the most reliable (Table III), is worthy of comment. The data selected are those of YOUNG [11]. For the determination of the pressure, YOUNG used an air manometer which was calibrated at a relatively low pressure [12]. The densities were determined in the same manner as in the present work, except that the length of the calibrated tube which was occupied by the sample, was measured on a millimetre scale etched on the tube. The same method was employed to obtain the volume of the air in the air manometer. These methods of measuring pressure and length are not as precise as those employed in this work and the difference in precision is believed to account for the difference in values of the vapour pressure and densities recorded in Table III.

ACKNOWLEDGMENT

Grateful acknowledgement is made to the American Cyanamid Company and to the Ohio State University for financial aid in the form

of fellowships to one of the authors during his period of graduate study. Acknowledgement is also made to the Lovejoy Memorial Fund for financial aid for the purchase of equipment.

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## Gas absorption by single drops during formation

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(Received 9 October 1954)

**Summary**—The amount of  $\text{SO}_2$  absorbed by individual drops of water and of several hydrocarbons has been measured continuously during their formation at the tip of a capillary tube. The times of formation varied between 1 and 40 seconds. A simplified calculation using the "penetration" theory explains the experimental results fairly well. At long formation times, however, the rate of absorption is somewhat increased by free convection currents, whereas at short times of formation a considerable increase in absorption rate may be found as a consequence of the mixing produced by the jet of liquid leaving the capillary. A tentative criterion for the occurrence of the latter effect is given.

**Résumé**—La quantité de  $\text{SO}_2$  absorbée par les gouttes individuelles d'eau et de plusieurs hydrocarbures a été mesurée d'une façon continue pendant leur formation à l'extrémité d'un tube capillaire. La période de formation de la goutte a été variée entre 1 et 40 secondes. Un calcul simplifié basé sur la théorie de la "pénétration" explique assez bien les résultats expérimentaux. Cependant, pour de longues périodes de formation, la vitesse d'absorption est augmentée légèrement par des courants libres de convection, tandis que à des périodes courtes de formation on peut trouver une augmentation considérable de la vitesse d'absorption par suite du mélange produit par le jet de liquide quittant le capillaire. On propose un critère déterminant la naissance de ce dernier effet.

### INTRODUCTION

The rate of mass transfer between a drop and a surrounding fluid has been subject to numerous experimental studies. In most of these experiments an extraction or absorption process has been carried out in a small-scale spray column. In such a process a distinction can be made between the exchange of material during the formation of the drop, during its free movement through the continuous phase and during coalescence. Generally, however, only the overall result of the exchange is measured. The sum of the beginning and end effects can then be estimated by extrapolation to zero drop life from results for the various times during which the free drop is in contact with its surroundings.

This procedure has been followed by SHERWOOD [1], LIGHT and CONWAY [2], and WEST *et al.* [3] for liquid-liquid extraction. Their results show that the rate of extraction during drop formation is relatively rapid. Quantitatively,

their data do not agree very well and they are contradictory as to the influence of the rate of formation of the drops on the initial extraction.

COULSON and SKINNER [4] have used a different method for measuring the initial extraction of a drop. They formed their drops on the tip of a jet, suspending them in the continuous phase, and let them disappear back into the same jet immediately after formation. They found smaller initial extraction rates than the previous workers. The same conclusion was reached by LIGHT and PANSING [5]. They showed that the extrapolation of extraction measurements according to SHERWOOD's [1] method may give values which are higher than the actual amount extracted during the growth of the drop; the release and subsequent vibration of the drop may account for an appreciable portion of the entire initial extraction effect.

Absorption of  $\text{CO}_2$  by water drops was investigated by WHITMAN [6] in a small column of

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constant height. He varied the time of formation and by extrapolation to zero formation time found the amount of gas absorbed during the free fall of the drop. Assuming this to be constant he calculated the absorption during formation by subtracting this constant value from the total amount absorbed. DIXON and RUSSELL [7], on the other hand, found that during the free fall of drops the rate of absorption of gas increased when the rate of formation of the drops was increased. They measured the initial effect by making the height of fall as small as possible, and found that under conditions of strong turbulence in the growing drop quite high absorption rates could occur.

The present investigation was undertaken to obtain a better understanding of the internal resistance of a drop to mass transfer during its formation. An experimental method was developed by which the amount of gas absorbed could be measured continuously during this period. To this end, drops were formed at the tip of a capillary in an enclosed volume containing pure  $\text{SO}_2$ . The amount of gas absorbed was determined by the measurement of pressure or volume changes. The results were compared with simple diffusion theory, which, for the sake of clarity, will be treated in the next section.

#### ABSORPTION BY A GROWING DROP

It is well known that the rate of diffusion of a solute into a semi-infinite, stagnant medium which has a concentration  $c = c_0$  at  $t = 0$  and a concentration  $c^*$  at its boundary for  $t > 0$ , is given by

$$N'' = (c^* - c_0) \sqrt{\frac{D}{\pi t}} \quad (1)$$

Here  $N''$  represents the rate of diffusion through the boundary per unit surface and  $D$  the coefficient of diffusion of the solute. This equation is also valid for diffusion into a layer of finite thickness, as long as the depth of penetration of the solute is relatively small. From this starting point, which has previously been used by HIGBIE [8] and DANCKWERTS [9] for treating gas absorption phenomena, it is possible to make a rough estimate of the absorption of gas by a drop being formed

at the tip of a capillary if the surrounding gas is not subject to diffusional resistance.

The surface area  $A$  of the drop increases with time. Let the area increment in the time interval between  $\theta$  and  $\theta + d\theta$  be  $dA(\theta)$ , then at the time  $t (> \theta)$  the rate of mass transfer through this area is:

$$dN = (c^* - c_0) \sqrt{\frac{D}{\pi(t-\theta)}} dA(\theta), \quad (2)$$

and the total rate of absorption at time  $t$ :

$$N(t) = (c^* - c_0) \sqrt{\frac{D}{\pi}} \int_{A(0)}^{A(t)} \frac{dA(\theta)}{\sqrt{(t-\theta)}}, \quad (3)$$

where  $A(0) = 0$ .

In this derivation it has been assumed that the depth of penetration is small compared with the radius of curvature of the surface, that there is no turbulence within the drop, and that the new surface being formed is really "fresh" surface with concentration  $c_0$ . The latter assumption is, of course, questionable, and entirely disregards possible diffusion parallel to the liquid surface.

For the case in which the drop is being formed at constant flow rate we have, for the volume of the drop:

$$V = \Phi_v \theta. \quad (4)$$

The relationship between  $V$  and the surface area  $A$  of the drop depends essentially on the conditions and the stage of formation. DIXON and RUSSELL [7] measured the volumes and areas of drops on capillary tips (2.8 mm O.D.), and found a reasonably constant ratio of volume to surface area. Since in the present investigation similar capillaries were used, it was considered justified to put

$$A = V/r_s \quad (5)$$

$r_s$  being a dimensional constant which was found to be 0.61 mm from DIXON and RUSSELL's data.

After substitution from (4) and (5), equation (3) can be integrated to give:

$$N(t) = \frac{2}{\sqrt{\pi}} (c^* - c_0) \frac{\Phi_v}{r_s} \sqrt{Dt}. \quad (6)$$

The amount of gas,  $m(t)$ , absorbed after a time  $t$  then follows from :

$$m(t) = \int_0^t N(t') dt' = \frac{4}{3\sqrt{\pi}} \frac{(c^* - c_0) \sqrt{D}}{r_e} \phi_v t^{3/2} \\ = \frac{4}{3\sqrt{\pi}} \frac{(c^* - c_0) \sqrt{Dt}}{r_e} V. \quad (7)$$

Consequently, the degree of saturation after a time  $t$  is :

$$\frac{\bar{c} - c_0}{c^* - c_0} = \frac{m(t)}{V(c^* - c_0)} = \frac{4}{3\sqrt{\pi}} \sqrt{\frac{Dt}{r_e^2}}. \quad (8)$$

#### EXPERIMENTAL PART

As can be seen from Fig. 1, the drops were formed at the end of a thick-walled glass capillary at a constant rate by displacing the liquid with mercury. In its turn the mercury was displaced by a plunger, which was pushed into the mercury by a mechanical drive. The flow rates could be adjusted by varying the thickness of the plunger and by using different plunger velocities. The volume of the drop at any stage of its formation could be derived from readings of the mercury level in the calibrated vertical tube (diam. about

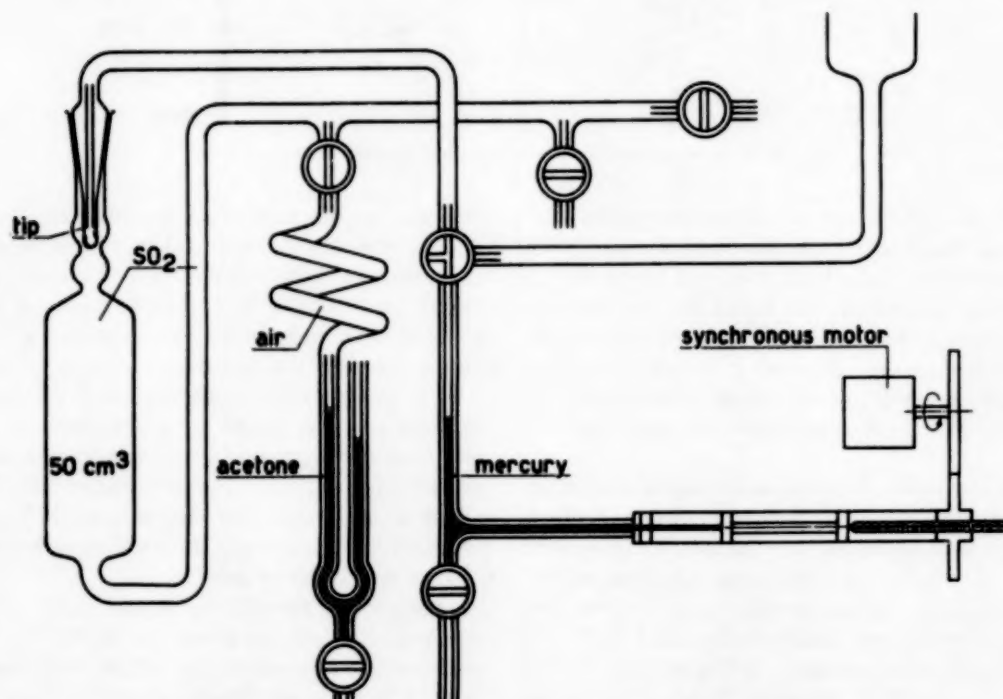


Fig. 1. Apparatus used for formation times longer than 5 seconds.

This relationship cannot be expected to be valid for relative saturation values greater than about 0.2, because the penetration of the solute then becomes too great and the assumption of a semi-infinite medium is no longer valid. In addition to this, the other assumptions have been such that equations (7) and (8) can be expected to have only qualitative significance.

1 mm).  $\text{SO}_2$  was used throughout the experiments as the gas to be absorbed. Only two capillaries were used :

- Tip No. 1, inner diameter 0.85 mm,  
outer diameter 2.6 mm
- Tip No. 2, inner diameter 0.35 mm,  
outer diameter 2.6 mm

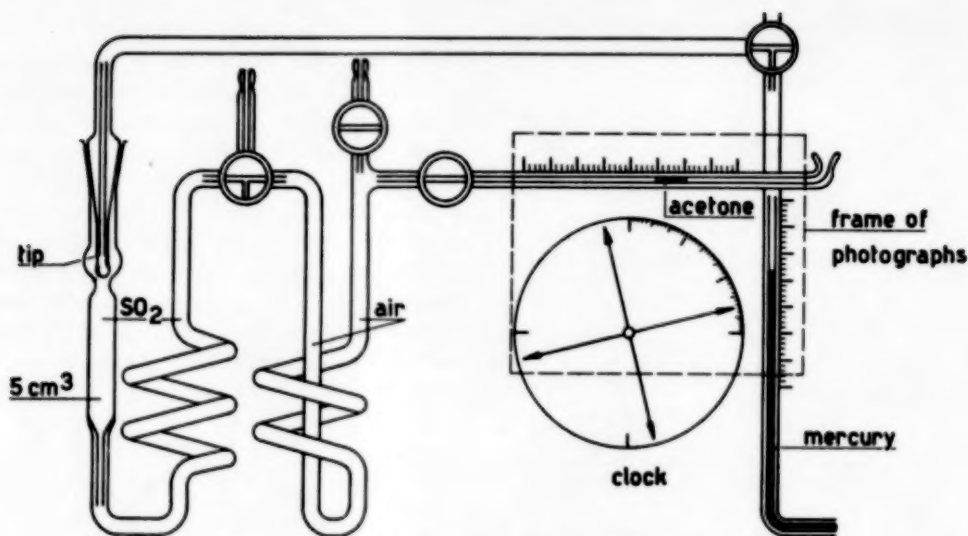


Fig. 2. Apparatus used for formation times shorter than 5 seconds.

The water drops fell off when their mass had become about 40 mg whereas the maximum drop mass of the hydrocarbons used was about 16 mg. Care was taken that the liquid did not wet the outer wall of the capillary; this was inevitable, however, with heptane and in a few cases with nonane, thereby causing much higher rates of absorption. Such results have not been reported here.

For low rates of formation (40 mg in more than 5 seconds) the vessel in which the absorption took place was connected with a manometer filled with acetone (Fig. 1). At the beginning of an experiment the absorption vessel, whose volume was accurately known, was entirely filled with  $\text{SO}_2$  gas which was saturated with respect to the liquid used. By measuring the pressure change occurring during the growth of the drop, the amount of  $\text{SO}_2$  absorbed could be calculated after correction for the drop volume. The pressure changes were always less than 10 cm of acetone.

For these slow runs the response time of the manometer proved to be negligible. When the drops were formed in less than 5 seconds, the amount of gas absorbed was determined by measuring the change of volume at constant pressure, which was indicated by the movement of a drop of acetone in a calibrated glass capillary

(Fig. 2). As the liquid experiments took 1 to 5 seconds photographs were taken of the position of the acetone drop and the level of the mercury column at intervals of  $1/16$ th second. A synchronous clock making one revolution in 5 seconds was included in the picture.

All measurements were carried out in triplicate, and only average results are given here. In the slow runs the reproducibility of  $m(t)$  proved to be well within 10%. For the fastest runs the spread in the results was larger than 10% in a few cases. The volumes absorbed were between 0.4 and 0.005  $\text{cm}^3$  of gas.

During a run the gas and liquid temperatures were kept constant (in general at  $20^\circ\text{C}$ ), but as a result of the absorption the drops were heated about 2 degrees centigrade above the ambient temperature. In view of the uncertainties involved in the theory and in the diffusion coefficients for the liquids, no attempt was made to take this temperature rise into consideration.

#### RESULTS WITH WATER DROPS

Fig. 3 shows a typical set of results for the weight of  $\text{SO}_2$  absorbed,  $m(t)$ , as a function of the time during which the drop was growing. It appears that the rate of absorption is higher for the shorter times of formation, but that the total



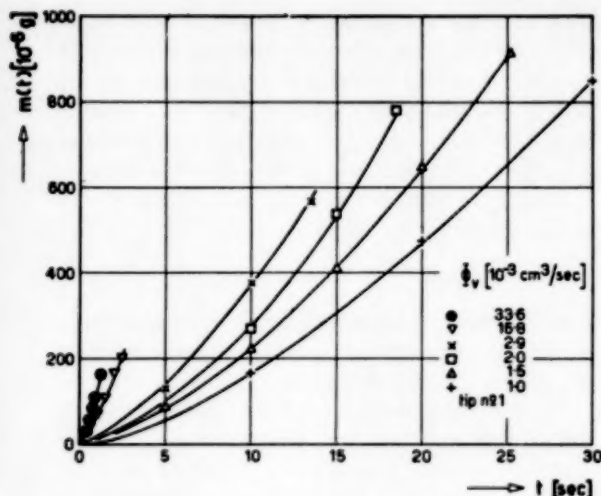


Fig. 3. Typical curves of the amount absorbed vs. time during drop formation; water.

amount absorbed is less than for the longer times of formation.

These data have been plotted in Fig. 4 as  $m(t)$  vs.  $Vt^{1/2}$ , in accordance with equation (7). The ratio of  $m(t)$  to  $Vt^{1/2}$  is very nearly constant, so that from these measurements a proportionality factor  $K$  can be derived:

$$\frac{m(t)}{Vt^{1/2}} = K. \quad (9)$$

According to the simple theory which has been derived above,  $K$  should be

$$K = \frac{4}{3\sqrt{\pi}} \frac{c^* - c_0}{r_e} \sqrt{D} \quad (9a)$$

and should thus be independent of the time of formation. From Fig. 4 it is seen, however, that  $K$  decreases for shorter times of formation.

The values of  $K_0$ , obtained for absorption by water with zero initial  $\text{SO}_2$  concentration, have been assembled in Table 1. This table shows that with slow formation there is no significant difference between the values of  $K_0$  obtained with the wide and with the narrow capillary.

In both cases a decrease in  $K$  is observed as the formation time becomes less. At high flow rates, however, the drop formed on tip No. 2 absorbs much faster than the drop on tip No. 1.

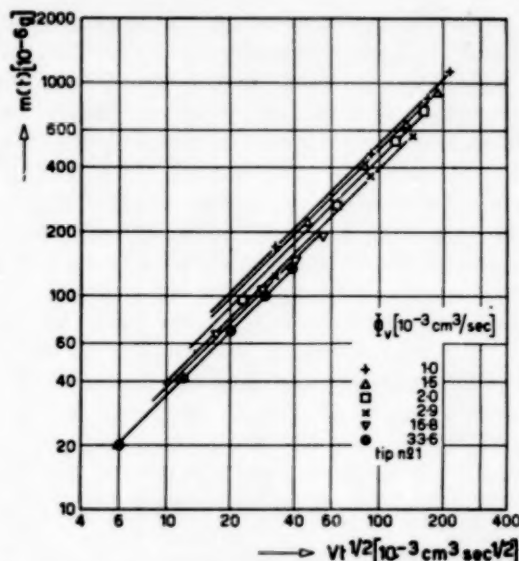


Fig. 4. Data of Fig. 3 plotted vs.  $Vt^{1/2}$  according to equation (7).

Table 1. Absorption of  $\text{SO}_2$  in growing water drops at  $20^\circ\text{C}$ .  $c_0 = 0$ .

$\Phi_v$ $10^{-3} \text{ cm}^3/\text{sec}$	$K_0, 10^{-3} \text{ g/cm}^3 \text{ sec}^{1/2}$		Approx. total formation time sec
	Tip No. 1	Tip No. 2	
1.0	5.1	5.4	40
1.5	5.1	5.3	27
2.0	4.8	4.5	20
2.9	4.1	4.6	14
4.0	3.9	4.1	10
8.0	3.8	3.7	5
16.8	3.4	4.2	2.4
33.6	3.5	5.1	1.2

This effect is caused by the greater circulation in the drop on tip 2, due to the jet of liquid leaving the narrow capillary.

The increase of  $K_0$  with decreasing values of  $\Phi_v$  can be ascribed to internal circulation in the drop in the reverse direction, which is due to density gradients. The density of a saturated solution of  $\text{SO}_2$  is 7% greater than that of water which is sufficient to cause appreciable convection

currents in these small drops. This was demonstrated by separate experiments in which phenolphthalein was added to water which had been made slightly alkaline. Since the water was decolorized upon absorbing the  $\text{SO}_2$  the flow pattern within the drop was made visible.

Fig. 5a shows an intermediate stage of absorption by a water drop hanging in  $\text{SO}_2$  gas (time of formation about 20 seconds). It is evident that there is sufficient time during the formation for the liquid containing  $\text{SO}_2$  to flow to the bottom of the drop. A similar photograph is shown in Fig. 5b; here a (rising) drop was formed in  $\text{CCl}_4$  which contained  $\text{SO}_2$ . It is rather surprising that with this convection taking place the proportionality between  $m(t)$  and  $Vt^{1/2}$ , derived from the very simple theoretical model given before, still obtains.

The intensity of free convection could be reduced by decreasing the difference in density between the surface and the bulk of the liquid by using a partially saturated solution of  $\text{SO}_2$  in water. The results are indicated in Table 2. From the last column it is seen that about 10% of the absorption rate at long formation times and  $c_0 = 0$  can be attributed to free convection.

Table 2. Absorption of  $\text{SO}_2$  in growing water drops having different initial  $\text{SO}_2$  concentrations at  $20^\circ\text{C}$ ;  $\phi_v = 1.5 \times 10^{-3} \text{ cm}^3/\text{sec}$ , Tip No. 1.

$C_0/C^*$	$K$ $10^{-3} \text{ g/cm}^3 \text{ sec}^{1/2}$	$K/(1 - \frac{C_0}{C^*})$ $10^{-3} \text{ g/cm}^3 \text{ sec}^{1/2}$
0	5.0 ( $K_0$ )	5.0
0.17	4.0	4.8
0.38	2.9	4.7
0.44	2.5	4.5
0.72	1.3	4.6
1.0	0	—

In order to check equation (9a) the following values were used: For  $c^*$  at  $20^\circ\text{C}$  the value of  $0.0995 \text{ g/cm}^3$  was taken as indicated by JOHNSTONE and LEPLA [10] for the equilibrium solubility of  $\text{SO}_2$  in water. Thus it was assumed that the hydration and subsequent partial ionization of  $\text{SO}_2$  in water are relatively fast. For

$D$ , the literature indicates values between 1.8 and  $1.5 \times 10^{-5} \text{ cm}^2/\text{sec}$ . Measurements by the authors (see also footnote to Table 4) on diffusion of  $\text{SO}_2$  into a stagnant water surface gave as a result:  $c^* \sqrt{D} = 0.87 \times 10^{-3} \text{ g/cm}^3 \text{ sec}^{1/2} \pm 5\%$ , yielding  $D = 1.4 \times 10^{-5} \text{ cm}^2/\text{sec} \pm 10\%$ . With these values,  $r_c = 0.061 \text{ cm}$  and  $C_0 = 0$ ,  $K_0$  is found to be according to equation (9a):

$$K_0 = 4.6 \times 10^{-3} \text{ g/cm}^3 \text{ sec}^{1/2}.$$

Thus the theory, in spite of its rough-and-ready character, provides a reasonable agreement with the  $K_0$ -values of Table 1.

From the dependence of  $c^*$  on temperature and the assumption that  $D$  is proportional to  $T/\mu$ , it can be calculated that  $K_0$  should be increased by nearly 2 per cent on lowering the temperature by  $1^\circ$  in the region between  $10^\circ$  and  $20^\circ\text{C}$ . This was confirmed by a number of measurements at  $10^\circ$ ,  $15^\circ$  and  $20^\circ\text{C}$ , the results of which are given in Table 3.

A few experiments in which a small amount of surface active agent was added to the water showed that this had no significant influence on the value of  $K$ . In these runs the final drop volume was of course smaller, owing to the lower surface tension.

#### ABSORPTION BY HYDROCARBON DROPS

Normal alkanes were used in order to vary the physical properties of the absorption system. Moreover, in these substances  $\text{SO}_2$  is only physically dissolved. Some properties of these liquids are given in Table 4.

The measurements of  $m(t)$  as a function of drop life gave results similar to those for water. In most cases  $m(t)$  proved to be exactly proportional to  $Vt^{1/2}$ . Only at high rates of formation with tip No. 2 did a plot of the data yield curves slightly convex to the  $Vt^{1/2}$ -axis. This can be ascribed to the fact that the jet of liquid from the capillary promotes the absorption more effectively in the initial stages than in the final stages of the drop formation. The least viscous liquid, *n*-heptane, behaved very exceptionally, giving a much faster absorption than was expected (up to 10 times the calculated rate for the short formation times). Unlike the other liquids, its surface was seen to



(a)



(b)

Fig. 5. Occurrence of free convection in absorption of  $\text{SO}_2$  in slowly formed water drops : (a) drop hanging in  $\text{SO}_2$  atmosphere, formation time about 20 sec.; (b) drop rising in  $\text{CCl}_4$  containing  $\text{SO}_2$ , formation time about 10 sec.

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# Gas absorption by single drops during formation

Table 3. Absorption of SO<sub>2</sub> in growing water drops at 10°, 15° and 20°C, c<sub>0</sub> = 0, Tip No. 1.

$\Phi_v$ 10 <sup>-3</sup> cm <sup>3</sup> /sec	$K_0$ (10°) × 10 <sup>3</sup>	$K_0$ (15°) × 10 <sup>3</sup>	$K_0$ (20°) × 10 <sup>3</sup>	$K_0$ (10°)/ $K_0$ (20°) meas. calc.	$K_0$ (15°)/ $K_0$ (20°) meas. calc.
1.0	—	5.52	5.16	—	1.07
1.5	5.76	5.73	4.98	1.16	1.15
2.0	—	4.75	4.61	—	1.03
2.9	4.74	4.34	4.00	1.19	1.09

Table 4. Properties of hydrocarbons (20°C).

Substance	Viscosity 10 <sup>-2</sup> g/cm sec	Solubility of SO <sub>2</sub> * g/cm <sup>3</sup>	Diffusivity of SO <sub>2</sub> ** 10 <sup>-5</sup> cm <sup>2</sup> /sec
n-heptane	0.41	0.0288	2.7
n-nonane	0.71	0.0265	2.5
n-decane	0.92	0.0250	2.4
n-dodecane	1.51	0.0226	2.0
n-hexadecane	3.34	0.0188	1.4

\* These values have been taken from earlier work done by the first author in the Koninklijke/Shell-Laboratorium, Amsterdam.

\*\* These values were determined experimentally from the rate of absorption of SO<sub>2</sub> exposed to a flat, fresh interface of the stagnant liquid. The equipment for measuring the rate of absorption was similar to that shown in Fig. 2. The diffusivities are thought to have an accuracy of ± 10%.

Table 5. Absorption of SO<sub>2</sub> in growing hydrocarbon drops at 20°C, c<sub>0</sub> = 0.

$\Phi_v$ 10 <sup>-3</sup> cm <sup>3</sup> /sec	Tip No.	$K_0$ , 10 <sup>-3</sup> g/cm <sup>3</sup> sec <sup>1</sup>			
		nonane	decane	dodecane	hexadecane
1.0	1	2.0	1.6	1.2	0.92
1.5	1	2.0	1.6	1.4	0.98
2.0	1	1.9	1.4	1.1	0.89
2.9	1	1.8	1.4	1.1	0.90
4.0	1	1.5	1.4	1.1	0.89
8.0	1	1.4	1.4	1.2	0.94
16.8	1	1.3	1.1	1.0	0.70
16.8	2	2.9	1.3	1.0	0.70
33.6	1	1.8	1.4	0.85	0.85
33.6	2	6.3	2.7	1.4	0.85
$K_0$ calculated, eq. (9a)		1.64	1.54	1.24	0.88

be in a state of high agitation during absorption. This effect was independent of the rate of formation.

Table 5 and Fig. 6, which summarize the results for the hydrocarbons, do not include the measurements with heptane.

The values of  $K_0$  for the hydrocarbons show the same trends as those observed for water: an increase with smaller values of  $\Phi_v$  (due to free convection) and with higher values of  $\Phi_v$  (due to jet mixing, especially noticeable with tip No. 2) with a minimum at intermediate rates of formation. Both effects tend to diminish as the viscosity increases. For hexadecane  $K_0$  is practically con-

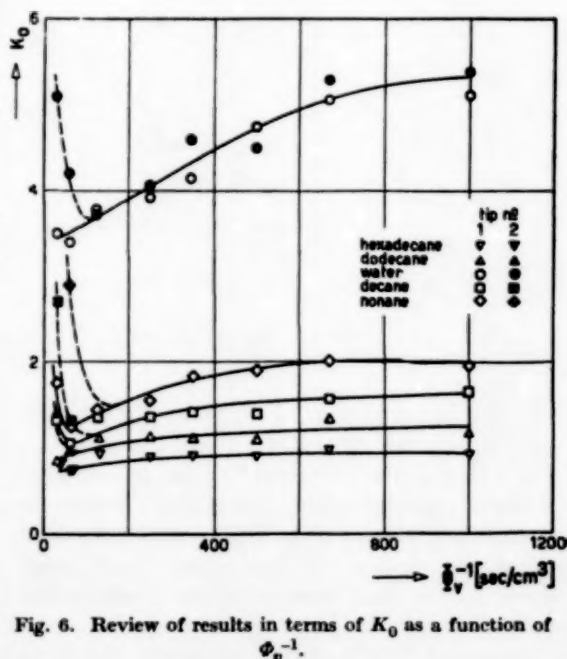


Fig. 6. Review of results in terms of  $K_0$  as a function of  $\Phi_v^{-1}$ .



stant. There is a rough agreement between the calculated and the measured values of  $K_0$ .

#### GENERAL DISCUSSION

All experimental results can be correlated according to equation (8) by plotting the relative saturation  $(\bar{c} - c_0)/(c^* - c_0)$  versus  $(Dt/r_e^2)^{1/2}$ . This has been done in Fig. 7, where the points indicate the degree of saturation for the moment at which

the observed phenomena. The effect of mixing by free convection and jet action can be seen to increase the relative saturation at long and at short formation times respectively, for the least viscous liquids. According to DIXON and RUSSELL's measurements, in the case of water  $r_e$  does not vary much with the outer diameter of the tip in the range between 0.2 and 0.8 cm. Thus equation (8) is believed to give a reasonable

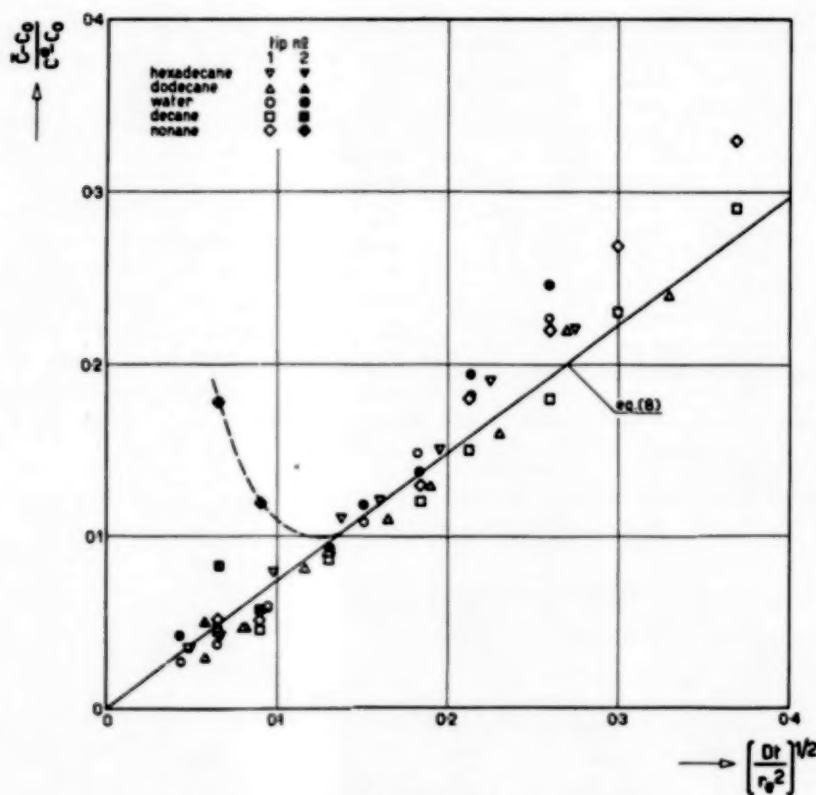


Fig. 7. Correlation of all results according to equation (8).

the drop has a volume of  $0.020 \text{ cm}^3$ . Thus each point is representative of an experimental run which would give a straight line passing through that point and the origin. The choice of  $0.020 \text{ cm}^3$  is arbitrary; it is about half the final volume of the water drops as they are released and about equal to the final volume of the hydrocarbon drops.

It appears that equation (8) roughly describes

estimate of the amount absorbed by a drop during its formation when the liquid side resistance is predominant and as long as the jet mixing effect is unimportant. The following criterion is proposed for the point at which the jet effect becomes important: the force exerted by the jet on the liquid in the drop is counteracted by viscous shear and by free convection due to density differences occurring during absorption.

If one neglects this effect of convection, one comes to the conclusion that the average velocity of the liquid leaving the capillary,  $\bar{u}$ , the viscosity of the liquid,  $\mu$ , the inner diameter of the capillary,  $d_i$ , and the drop size must be the most important factors affecting the jet action. In these measurements  $\bar{u}$  varied from 0.2 to 35 cm/sec and  $\mu$  from 0.7 to 3.3 cP;  $d_i$  was either 0.085 or 0.035 cm. From the reported data it was found that for a value of

$$\frac{\rho \bar{u} d_i}{\mu} > 40 \text{ to } 50$$

the rate of absorption begins to increase as a result of jet action. Whether there is also an influence of the average drop size cannot be determined from these data since the outer diameter of the capillary tube was not changed.

DIXON and RUSSELL [7] expressed the "degree of turbulence" in their growing drops in terms of  $1/d_i$  at constant formation time (roughly constant  $\Phi_e$ ). This is not in contradiction to the dimensionless criterion mentioned above. By analysing their reported data one can find that above a value of  $\rho \bar{u} d_i/\mu$  of about 50 the rate of  $\text{CO}_2$  absorption increases when the formation time is kept constant. However, the relative saturation found by them for "quietly" formed drops is about twice the value calculated by means of equation (8). This is probably due to

the fact that in their results the absorption during release of the drop is included, whereas in the measurements reported here only absorption during growth was measured.

#### ACKNOWLEDGMENT

The first author wishes to thank the management of the the Koninklijke/Shell-Laboratorium, Amsterdam (N.V. De Bataafsche Petroleum Maatschappij), for the opportunity given to him for carrying out this work.

#### NOTATION

$A$	= surface area ( $\text{cm}^2$ )
$c$	= concentration of $\text{SO}_2$ in liquid ( $\text{g}/\text{cm}^3$ )
$\bar{c}$	= mean concentration
$c_0$	= initial concentration
$c^*$	= saturation concentration
$d_i$	= inner diameter of capillary tube
$D$	= coefficient of diffusion of $\text{SO}_2$ in liquid ( $\text{cm}^2/\text{sec}$ )
$K$	= constant defined by equation (9); $K_0$ for $c_0 = 0$
$m(t)$	= amount of $\text{SO}_2$ absorbed after $t$ sec (g)
$N''$	= diffusion rate ( $\text{g}/\text{cm}^2 \text{ sec}$ )
$N$	= absorption rate ( $\text{g}/\text{sec}$ )
$r_s$	= $V/A$ for growing drops, here 0.061 cm
$t$	= time (sec)
$T$	= absolute temperature ( $^\circ\text{K}$ )
$\bar{u}$	= average linear velocity ( $\text{cm}/\text{sec}$ )
$V$	= volume of liquid drop ( $\text{cm}^3$ )
$\mu$	= dynamic viscosity ( $\text{g}/\text{cm sec}$ )
$\rho$	= liquid density ( $\text{g}/\text{cm}^3$ )
$\theta$	= variable time (sec)
$\Phi_e$	= volumetric rate of liquid flow ( $\text{cm}^3/\text{sec}$ )

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## The use of a sedimentation cell in the sampling of aerosols

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(Received 27 August 1954)

**Summary**—The limited range of conditions under which a reliable sample is obtained are discussed, and recommendations are made for the design of the cell.

**Résumé**—Les auteurs discutent l'étendue limitée de conditions dans lesquelles on peut obtenir un échantillon valable et donnent des conseils pour le projet de la cellule.

### 1. INTRODUCTION

The sedimentation cell has long been considered a reliable means of sampling an aerosol and has been used as a standard in the appraisal of other sampling devices [1], [2]. It is generally constructed so that a volume of aerosol can be enclosed and then allowed to settle on to a glass slide at the bottom of the cell. The particles can later be examined and counted with the aid of a microscope.

The cell used in the present work is shown diagrammatically in Fig. 1 and was similar to

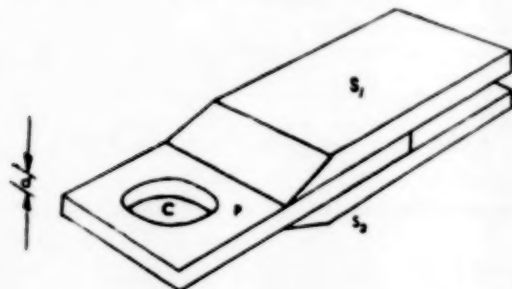


Fig. 1

that described by WHYTLOW-GRAY and PATTERSON [3]. It consists of a spacer *P* with a circular orifice *C*, and two slides *S*<sub>1</sub> and *S*<sub>2</sub> which are moved simultaneously to isolate a sample of aerosol; a glass plate is fitted in the lower slide *S*<sub>2</sub>.

The cell was found to suffer from certain

limitations which had not previously been reported.

### 2. RANGE OF APPLICATION

The various sampling errors which can occur during use of the instrument will now be discussed and the range of conditions over which it gives a representative sample will be indicated.

2.1. When particles settle at random on a horizontal surface, a certain fraction  $\epsilon$  overlap one another. ARMITAGE [4] has shown that when  $n_1$  identical circular discs of radius  $a$  fall at random on unit area:

$$\epsilon = 1 - 2\pi n_1 a^2 + \text{terms in } (n_1 a^2)^2 \text{ etc.} \quad (1)$$

Thus if the particles are deposited from a column of height  $d$  of aerosol of numerical concentration  $n$

$$\epsilon \approx 1 - 2\pi a^2 nd \quad (2)$$

provided only a small proportion of the area is covered by particles.

If  $\epsilon_1$  is the largest permissible fraction of particles overlapping, the depth of the cell must be not greater than:

$$d = (1 - \epsilon_1)/2\pi a^2 n \quad (3)$$

2.2. The sample on the slide will not be representative if an appreciable proportion of the aerosol settles as the cell is closed.

In Fig. 2, a particle of radius  $a$  and settling velocity  $v$  is shown initially near the leading edge of the upper surface of the cell. If the slide is

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closed with a velocity  $u$ , the particle strikes the lower surface at a distance  $x$  from its leading edge, where :

$$x = u d / v \quad (4)$$

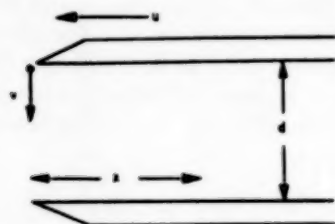


Fig. 2

and the distribution of particles over the slide is not uniform. If the diameter of the cell is  $2r$ , the time of closing is  $2r/u$  and an element of the slide at a distance  $x$  from the leading edge is exposed for a time  $(2r - x)/u$ . The number of particles deposited per unit area at  $x$  is then  $n v (2r - x)/u$ , and at the instant of closure  $n (d - x v/u)$  particles per unit area are still to be deposited. Hence the total deposition  $N$  per unit area at  $x$  is :

$$N = n [d + 2 (r - x) v / u] \quad (5)$$

for values of  $x$  less than  $r + u d / 2r$ . At greater distances there is no deposition.

If the aerosol is polydisperse,  $n$  and  $v$  are functions of the radius  $a$  of the particles, and the number deposited per unit area at  $x$  is :

$$N = n(a) [d + 2 (r - x) v(a) / u] \quad (6)$$

where  $n(a)$  is the numerical concentration of particles of radius  $a$  and  $v(a)$  is their sedimentation velocity. An example of the distribution obtained in a sample of an oil mist is shown in Fig. 3.

The numerical concentration  $n$  in the aerosol can be determined graphically from the intercepts on the axis in Fig. 3 since :

$$n = N_0 (1 - 2 r / x_1) / d \quad (7)$$

where  $N_0$  is the intercept on the  $N$  axis and  $x_1$  is that on the  $x$  axis.

2.3. Although it would appear from equation (4) that the rate of closing  $u$  should be as high as possible, excessively rapid movement of the slides can cause turbulence with the result that particles are deposited on the walls and the upper slide, giving an uneven distribution as shown in Fig. 3.

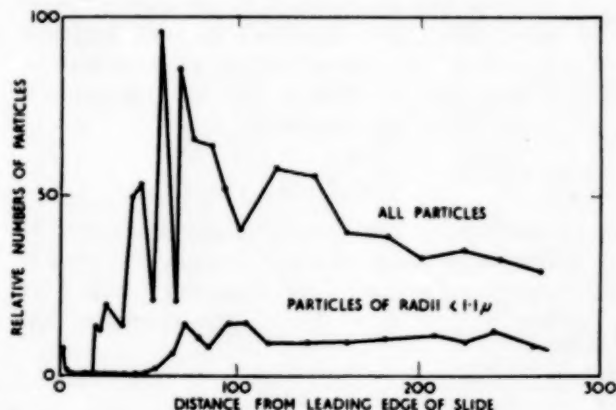


Fig. 3

2.4. The sample will not be representative if an appreciable proportion of the aerosol diffuses to the walls of the cell. As the diameter of the cell is arranged to be very much greater than its depth, only the top and bottom surfaces need be considered. With material of density 1 gram per cu. cm in a shallow cell, this loss becomes significant with particles less than about 0.5 microns in radius.

The depth  $d$  of the cell should in any case be so chosen that it is at least ten times as great as the root mean square displacement of the particle  $(\bar{y}^2)^{1/2}$  due to its Brownian motion during the sedimentation period,  $t$ . Since  $t = \frac{d}{v}$  and  $\bar{y}^2 = 2 D t$ , from EINSTEIN'S equation [5], the minimum depth for the cell is given by

$$d = 200 \frac{D}{v} = 200 \frac{kT}{mg} \quad (8)$$

since  $D = \frac{kT}{6 \pi a \eta}$  and  $v = \frac{mg}{6 \pi a \eta}$ ,

where  $k$  is Boltzmann's constant  
 $T$  is absolute temperature  
 $g$  is the acceleration due to gravity  
 $m$  is the mass of the particle  
 $a$  is the radius of the particle  
 $\eta$  is the viscosity of the gas.

2.5. When the aerosol is composed of liquid droplets, they may spread. If a droplet is treated as a plano-convex lens and its focal length is measured, the true radius may be calculated by a method due to MAY [6], provided the radius is more than about 5 microns.

### 3. DESIGN OF THE CELL

An estimate must first be made of the concentration of the aerosol and equation (8) used to calculate the maximum depth for which overlapping is inappreciable. If this is greater than

the minimum depth given by equation (8) the method of sampling is feasible, i.e., if :

$$(1 - \epsilon_1)/2\pi a^2 n > 200 kT/mg \quad (9)$$

To prevent loss of larger particles near the leading edge, the diameter of the cell should be greater than  $ud/v$  (from equation 4). For the purpose of calculation, the speed of closing must be estimated. A large diameter is advantageous since the loss of particles to the side walls is reduced.

### ACKNOWLEDGMENTS

The authors wish to thank Professor D. M. NEWITT for his supervision of the work. They are indebted to the British Shipbuilding Research Association who sponsored the researches during which the sedimentation cell was examined. This paper appears with the Association's permission.

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## On the steady state fractionation of multicomponent and complex mixtures in an ideal cascade

### Part I—Analytic solution of the equations for general mixtures

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(Received 6 October 1954)

**Summary**—The equations for the steady state rectification of mixtures which obey a rather general vapour-liquid equilibrium law in an ideal cascade are solved in closed form. Various kinds of mixtures are examined. From the mathematical standpoint the problem presents some interesting features, first, because it may be linearized and, second, it can be reduced to an eigenvalue problem which in turn can be solved by a new transform, the transform being finite or infinite depending upon the number of components in the mixture. Methods for the numerical evaluation of the formulae as well as applications to practice will be reported elsewhere. The calculation of the minimum reflux will be presented in Part II.

**Résumé**—Dans le cas d'une cascade idéale, l'auteur a résolu les équations de la rectification en état stationnaire de mélanges qui obéissent à une loi d'équilibre liquide-vapeur suffisamment générale. Il examine diverses sortes de mélanges. Du point de vue mathématique, le problème présente quelques caractéristiques intéressantes : (1°) parce qu'il peut être mis sous forme linéaire et (2°) parce qu'il peut être ramené à un problème "de valeurs particulières" qui peut être résolu, à son tour, par une nouvelle transformation, cette transformation étant finie ou infinie, suivant le nombre de composants du mélange. L'auteur donne-ra ailleurs des méthodes pour l'évaluation numérique des formules aussi bien que des applications pratiques. Il présentera le calcul du reflux minimum dans la deuxième partie.

#### 1. INTRODUCTION

To be able to design a fractionating column, or cascade, and to predict its behaviour at steady state has been a well known problem which is still far from solved. Considerable progress towards the eventual solution of this problem has been made during the past years and many of the factors which influence the operation of cascades are beginning to become clearer and to be understood. It still remains true, nevertheless, that the physical model itself is too involved to be treated exactly and it is for this reason that several mathematical models have been constructed and used with some success. It is the purpose of this paper to exhibit solutions of the most commonly used model, the ideal column. From a mathematical standpoint the problem has some interesting features because the methods

employed to solve the basic equations for the ideal column are both rather unusual and sometimes even intriguing. Methods for the numerical evaluation of the formulae will be reported elsewhere.

#### 2. THE IDEAL COLUMN.

##### THE BASIC EQUATIONS FOR THE RECTIFICATION OF DISCRETE MIXTURES

A simple cascade can be represented schematically by Fig. 1. Vapour travels up the column and liquid moves in the downward direction the two being contacted in stages so that the two streams leaving a stage are in equilibrium, more or less. The column can be divided into two sections, the upper part or enriching section and the lower part, or stripping section, the two sections being separated by the introduction of the feed. For

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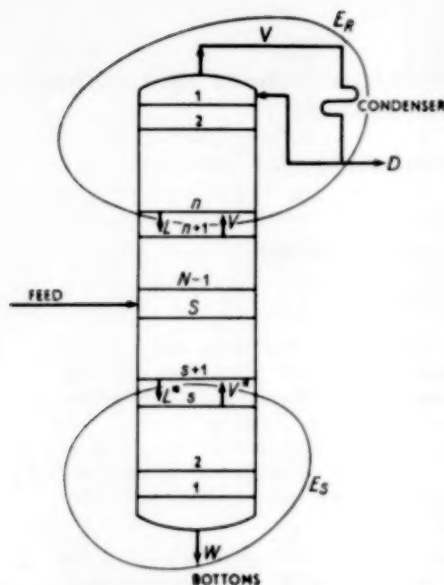


Fig. 1. Schematic diagram of a distillation cascade.

the moment, only discrete mixtures, that is, mixtures with a finite number of distinguishable components, will be considered. By a mass balance around the envelope  $E$ , the following equation is obtained,

$$y_{n+1}(i) = \frac{L_n}{V_{n+1}} x_n(i) + \frac{D}{V_{n+1}} x_0(i) \quad (2.1)$$

where

$y_{n+1}(i)$  = mole fraction of the  $i$ th component in the vapour stream leaving the  $(n+1)$ th stage.

$x_n(i)$  = mole fraction of the  $i$ th component in the liquid stream leaving the  $n$ th stage.

$L_n$  = moles of liquid leaving  $n$ th stage.

$V_{n+1}$  = moles of vapour leaving  $(n+1)$ th stage.

$D$  = moles of overhead stream.

$x_0(i)$  = mole fraction of  $i$ th component in the overhead stream.

It will be assumed that the streams leaving a single stage are in thermodynamic equilibrium

and that the equilibrium is described by the equation\*

$$x_n(i) = \frac{p_n(i) y_n(i)}{\sum p_n(i) y_n(i)} \quad (2.2)$$

where  $p_n(i)$  is related to the vapour pressure of the component, the vapour-liquid equilibrium constant, or the relative volatility, and  $m$  denotes the total number of components in the mixture. Combining Eqs. (2.1) and (2.2) there results

$$y_n(i) = \frac{R_n}{1 + R_n} \frac{p_n(i) y_n(i)}{\sum p_n(i) y_n(i)} + \frac{x_0(i)}{1 + K_n} \quad (2.3)$$

where

$$V_{n+1} = L_n + D$$

$$L_n = R_n D \quad (2.4)$$

It will be seen from the above equations that there are two independent variables, namely,  $i$  and  $n$ , where  $i$  is the component designating variable and  $n$  denotes the stage number. Certainly  $i$  and  $n$  are integers such that  $1 \leq i \leq m$  and  $n \geq 0$ ,  $n = 0$  denoting the condensing stage.

Now, in general, Eq. (2.3) is misleading to the extent that  $R_n$  and  $p_n(i)$  are functions not only of  $n$  but also of the temperature and composition of the liquid mixture in each stage. To take this into consideration in an analytical way presents insurmountable difficulties so that the model will be simplified further: viz., it will be assumed that  $p_n(i) = p(i)$  for all  $n$  and  $R_n = R$  for all  $n$ . The basic equation, then, which must be solved is given by

$$y_{n+1}(i) = \frac{R}{R+1} \frac{p(i) y_n(i)}{\sum p(i) y_n(i)} + \frac{x_0(i)}{R+1} \quad (2.5)$$

and it is desired to obtain an analytic expression for  $y_n(i)$  subject to the condition that

$$y_1(i) = x_0(i) \quad (2.6)$$

a self evident relation, which is valid whenever a total condenser is used. This model, although somewhat restrictive in nature, holds for a wide class of mixtures such as isotopes and hydrocarbons. Its use in many cases is of doubtful

\* Summations are over the components in the mixture from 1 to  $m$ .  $\Sigma$  denotes that an obvious term must be omitted from the summation.

value for precise results, but, as in the case of all analytic formulae, the qualitative and asymptotic deductions are important. A detailed discussion of cascades and distillation processes may be found in a wide variety of references. The solution of Eq. (2.5) will now be found for discrete mixtures. The solution for non-discrete mixtures will be found later in the paper.

### 3. THE SOLUTION OF THE PROBLEM FOR DISCRETE MIXTURES

1. The general solution of the equations for the enriching section. Our first task is to linearize Eq. (2.5). If one considers the equation for  $n=1$ , then it follows that

$$y_2(i) = \frac{R}{R+1} \frac{p(i) x_0(i)}{\sum p(i) x_0(i)} + \frac{x_0(i)}{R+1}$$

If in this formula alone  $p(i)$  is replaced by  $Y_1(i)$  and  $y_2(i)$  is substituted into the expression for  $y_3(i)$  there results

$$\begin{aligned} p(i) y_2(i) &= \frac{1}{R+1} \frac{x_0(i) [R p(i) Y_1(i) + p(i) \sum Y_1(i) x_0(i)]}{\sum Y_1(i) x_0(i)} \\ p(i) y_3(i) &= \frac{1}{R+1} \frac{x_0(i) [R p(i) Y_2(i) + p(i) \sum Y_2(i) x_0(i)]}{\sum Y_2(i) x_0(i)} \\ &= \frac{1}{R+1} \frac{x_0(i) Y_3(i)}{\sum Y_2(i) x_0(i)} \end{aligned}$$

if  $Y_3(i)$  is defined to be

$$Y_3(i) = R p(i) Y_2(i) + p(i) \sum Y_2(i) x_0(i)$$

Hence it is clear that if one defines

$$Y_{n+1}(i) = p(i) R Y_n(i) + p(i) \sum Y_n(i) x_0(i)$$

then

$$p(i) y_n(i) = \frac{1}{R+1} \frac{x_0(i) Y_n(i)}{\sum Y_{n-1}(i) x_0(i)}$$

It is convenient for later work to have  $Y_n(i) = R X_n(i)$  so that

$$p(i) y_n(i) = \frac{1}{R+1} \frac{X_n(i) x_0(i)}{\sum x_0(i) X_{n-1}(i)} \quad (3.1)$$

and

$$X_{n+1}(i) = R p(i) X_n(i) + p(i) \sum x_0(j) X_n(j) \quad (3.2)$$

It is to be noted here that Eq. (3.2) is an equation of partial differences to which must be appended the condition

$$X_1(i) = \frac{p(i)}{R} \quad (3.3)$$

Thus the solution of the non-linear difference equation, Eq. (2.5), may be solved once the solution to the linear difference equation, Eq. (3.2) has been found. Equation (3.2) may be solved since it may be written

$$X_{n+1}(i) = H X_n(i) \quad (3.4)$$

where  $H$  is a linear operator. The iterative method applies and the solution is

$$X_n(i) = \frac{1}{R} H^{n-1} p(i) \quad (3.5)$$

an expression which is rather cumbersome to apply. This iterative solution is identical with what is commonly called the "plate by plate" method.

If one assumes the variables in Eq. (3.2) may be separated then  $X_n(i) = v(i) N(n)$  and

$$v(i) N(n+1) = R p(i) v(i) N(n) + p(i) \sum v(i) N(n) x_0(i)$$

and

$$\frac{N(n+1)}{N(n)} = \frac{R p(i) v(i) + p(i) \sum v(i) x_0(i)}{v(i)}$$

By the usual argument

$$N(n+1) = R \lambda N(n)$$

and

$$H v(i) = R p(i) v(i) + p(i) \sum_1^m v(i) x_0(i) = R \lambda v(i)$$

where  $R \lambda$  has been chosen as the representation for the eigenvalue. Therefore if it is assumed, for the moment, that there are  $q$  eigenvalues then the solution may be written in the form

$$X_n(i) = \sum_{k=1}^q C_k (R \lambda_k)^{n-1} v_k(i) \quad (3.6)$$

$v_k(i)$  being the representation for the  $k$ th eigenfunction. Also since

$$v_k(i) = \frac{p(i)}{R [\lambda_k - p(i)]} \sum x_0(j) v_k(j)$$

it follows that if this formula is multiplied by  $x_0(i)$  and summed on  $i$  from 1 to  $m$ , then

$$\sum \frac{p(i)x_0(i)}{\lambda - p(i)} = R. \quad (3.7)$$

This equation determines the eigenvalues and since  $p(i)$  is assumed to be a single valued function of  $i$  for the discrete case, there are  $m$ ,  $q = m$ , distinct eigenvalues all of which are real and positive as shown by the intersections on Fig. 2.

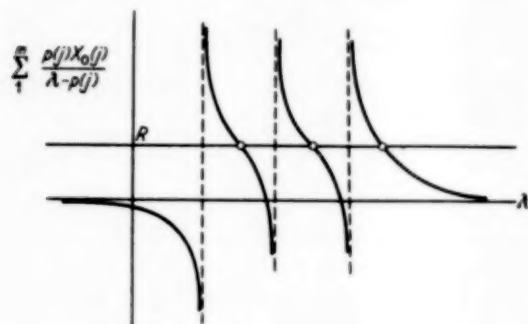


Fig. 2. Qualitative plot of equation for determination of eigen values.

It is clear that  $v_k(i)$  may be defined by

$$v_k(i) = \frac{p(i)}{\lambda_k - p(i)} \quad (3.8)$$

From (3.7) and (3.8) it follows that

$$(v_k, v_{k'}) = \delta_{kk'} \sum \frac{p(j)x_0(j)}{\lambda_k - p(j)} \quad (3.9)$$

where  $\delta_{kk'}$  is the Kronecker symbol and the inner product  $(v_k, v_{k'})$  is defined by

$$(v_k, v_{k'}) = \sum \frac{x_0(j)}{p(j)} v_k(j) v_{k'}(j) \quad (3.10)$$

Thus the eigenvalues are non-degenerate and the eigenfunctions form an orthogonal set. That the set is complete can be readily proved, for if  $f(i)$  is an arbitrary function of  $i$  defined at  $i = 1, 2, \dots, m$  then it can be expanded in terms of the eigenfunctions  $v_k(i)$ , i.e.,

$$f(i) = \sum_{k=1}^m c_k v_k(i)$$

for  $1 \leq i \leq m$ . The above is but a set of  $m$

linearly independent linear equations in  $m$  unknowns and so possesses a unique solution in the  $c_k$ 's since the eigenfunctions are linearly independent. In order to determine the  $C_k$ 's in Eq. (3.6) it need be noted only that

$$X_1(i) = \frac{p(i)}{R} = \sum_{k=1}^m C_k v_k(i).$$

Hence

$$C_k = (v_k, v_k)^{-1} \quad (3.11)$$

It can easily be shown from Eqs. (3.1) and (3.2) that

$$x_n(i) = \frac{x_0(i) X_n(i)}{\sum x_0(i) X_n(i)} \quad (3.12)$$

and therefore

$$x_n(i) = \frac{x_0(i)}{R} \frac{\sum_{k=1}^m C_k \lambda_k^{n-1} v_k(i)}{\sum_{k=1}^m C_k \lambda_k^{n-1}} \quad (3.13)$$

Eq. (3.13) represents the solution of the problem originally posed.

Thus far the one to one correspondence of the symbol  $i$  and the component in the mixture has been left arbitrary. For convenience the  $p(i)$  will be ordered so that

$$p(1) > p(2) > p(3) > \dots > p(m).$$

The eigenvalues will also be ordered in such a way that

$$p(k) < \lambda_k < p(k-1)$$

and from Fig. 2 this is clearly possible.

2. *The stripping section.* The equations for the stripping section are essentially identical with those of the enriching section. It can readily be shown that

$$y_{r-1}^* = \frac{R^*}{R^* - 1} \frac{p^*(i) y_s^*(i)}{\sum p^*(i) y_s^*(i)} - \frac{x_0^*(i)}{R^* - 1} \quad (3.14)$$

where  $L^* = R^*W$  and  $x_0^*(i)$  is the mole fraction of the  $i$ th component in the liquid mixture leaving the zeroth plate (reboiler) at the bottom of the cascade. For the sake of generality it has been assumed that  $p(i)$  is different in the two sections of the column,  $p(i) \neq p^*(i)$ . Eq. (3.14) can be solved in the same manner as (2.5) and it is found that

$$x_i^*(i) = \frac{x_0^*(i) \sum_{k=1}^m C_k^* \phi_k^{i-1} v_k^*(i)}{R^* \sum_{k=1}^m C_k^* \phi_k^{i-1}} \quad (3.15)$$

where

$$v_k^*(i) = \frac{p^*(i)}{p^*(i) - \phi_k} \quad (3.16)$$

and the  $\phi_k$ 's are the  $m$  roots of

$$\sum_{k=1}^m \frac{p^*(j) x_0^*(j)}{p^*(j) - \phi_k} = R^* \quad (3.17)$$

ordered in such a way that

$$p^*(k+1) < \phi_k < p^*(k)$$

and

$$C_k^* \sum_{j=1}^m \frac{p^*(j) x_0^*(j)}{[p^*(j) - \phi_k]^2} = 1 \quad (3.18)$$

Finally at the plate where the raw feed is introduced, where  $n = N$  and  $s = S$ , one must have

$$x_N(i) = x_S(i)$$

or by combining (3.13) and (3.15)

$$\frac{x_0(i) \sum_{k=1}^m C_k \lambda_k^{N-1} v_k(i)}{R \sum_{k=1}^m C_k \lambda_k^{N-1}} = \frac{x_0^*(i) \sum_{k=1}^m C_k^* \phi_k^{N-S-1} v_k^*(i)}{R^* \sum_{k=1}^m C_k^* \phi_k^{N-S-1}} \quad (3.19)$$

If  $x_F(i)$  denotes the mole fraction of the  $i$ th component of the feed, then by a mass balance around the whole cascade (per mole of feed)

$$x_F(i) = D x_0(i) + W x_0^*(i) \quad (3.20)$$

From Eqs. (3.19) and (3.20) it is apparent that one cannot specify a priori either  $x_0(i)$  or  $x_0^*(i)$ . As a matter of fact, if  $R$ , the composition of the feed and its thermal condition are given and if it is stated, moreover, that the feed is to be introduced at such a plate in the column as to make the total number of plates for a given separation a minimum, then it is easy to show that there are two degrees of freedom remaining, irrespective of the number of components in the mixture. These are

normally exhausted by specifying  $x_0(i)$  at  $i = \beta$  and  $x_0^*(i)$  at  $i = \beta^*$ .

3. A useful asymptotic expression. A useful asymptotic form for  $x_N(i)$  can be obtained if  $x_0(i)$  is made small. First the function

$$w(i) = R - \sum_j \frac{p(j) x_0(j)}{p(i) - p(j)} \quad (3.21)$$

is defined. Now if  $w(i) > 0$ , which is generally the only case of interest, and if  $x_0(i)$  is small, then

$$\lambda_i = p(i) \left( 1 + \frac{x_0(i)}{w(i)} \right) \quad (3.22)$$

provided that

$$R - \sum_j \frac{p(i) x_0(j)}{p(i) - p(j) + \frac{p(i) x_0(i)}{w(i)}} \simeq w(i) - \frac{p(i) x_0(i)}{w(i)} \sum_j \frac{p(j) x_0(j)}{[p(i) - p(j)]^2} \simeq w(i)$$

or, more precisely, that

$$\frac{p(i) x_0(i)}{w(i)} \left( - \frac{\partial w(i)}{\partial p(i)} \right) < < w(i) \quad (3.23)$$

Also

$$\sum_j \frac{p(j) x_0(j)}{[\lambda_i - p(j)]^2} \simeq \frac{[w(i)]^2}{p(i) x_0(i)} + \sum_j \frac{p(j) x_0(j)}{[p(i) - p(j)]^2} = \frac{[w(i)]^2}{p(i) x_0(i)} - \frac{\partial w(i)}{\partial p(i)}$$

and if (3.23) is satisfied, then from the above and (3.11) it follows that

$$C_i = \frac{p(i) x_0(i)}{[w(i)]^2} \quad (3.24)$$

provided that  $x_0(i)$  is sufficiently small. In addition, if

$$x_0(i) \sum_{k \neq i} C_k \lambda_k^{N-1} v_k(i) < < w(i) C_i \lambda_i^{N-1} \quad (3.25)$$

then one easily obtains from the above and (3.13)

$$x_N(i) = \frac{p(i) x_0(i) \lambda_i^{N-1}}{R w(i)} [\sum C_k \lambda_k^{N-1}]^{-1} \quad (3.26)$$

Equation (3.26) is an asymptotic expression which is valid only if  $x_0(i)$  is sufficiently small so that Eqs. (3.23) and (3.25) are satisfied, and if  $w(i) > 0$ . Naturally, an entirely analogous asymptotic formula holds for  $x_S^*(i)$  if  $x_0^*(i)$  is sufficiently small.



Thus far the separation of mixtures with a finite number of components in an ideal cascade has been examined and the basic equation (2.5) has been solved analytically without recourse to approximations. Similar problems have been discussed by HERBERT [1], UNDERWOOD [2], MURDOCH [3], HIRAYAMA [4], and the present authors [5], by different methods. It is felt that the present method is more straightforward and has the particular advantage that it may be extended to more complex mixtures and in particular to mixtures which have a continuous distribution function.

#### 4. THE SOLUTION OF THE PROBLEM FOR COMPLEX MIXTURES

1. *Continuous Mixtures.* In recent years the theoretical treatment of the separation of mixtures with an indefinite number of components, that is, where the concentration of the various components can be approximated by a distribution curve, has received some attention. BOWMAN [6] was the first to transform the equations which describe a state for a discrete number of components so that they could equally well apply for the continuous case; he then used those equations to study some systems, namely, batch distillation and flash vapourization [7]. It is the purpose of the latter part of this paper to present BOWMAN's equations for the rectification of mixtures with an indefinite number of components and to solve those equations both by the iterative method and by a scheme analogous to that presented earlier and involving the use of a new integral transform. The theoretical treatment, aside from its mathematical interest, will be found useful in studying the rectification of petroleum mixtures and, in many instances, accurate enough to be used in the discrete case where the number of components is so large that the equations developed earlier would be somewhat cumbersome to use.

It will be supposed that each component in the continuous mixture is present in infinitesimal amount. For discrete mixtures the component designating variable was the integer  $i$  in  $p(i)$ . For continuous mixtures it is natural to employ the quantity  $p$  itself as the variable designating the

component since this is, in general, unique at a fixed temperature and pressure. It is apparent that the mole fraction cannot be used to specify the composition of a mixture but it is much more convenient to specify the composition of the mixture by a distribution function, defined as follows: Let  $x_n(p) dp$  be the mole fraction in the liquid phase leaving the  $n$ th stage of material having  $p$  values between  $p$  and  $p + dp$ . The vapour distribution function is defined analogously. Methods for calculating the distribution function of a given mixture from its experimentally obtained true boiling curve have been exhaustively discussed by HERBERT [8] and BOWMAN [9]. The conditions

$$\int_0^{\infty} x_n(p) dp = 1 \quad (4.1)$$

$$\int_0^{\infty} y_n(p) dp = 1 \quad (4.2)$$

are self evident. Further conditions to be imposed on  $x_n(p)$  and  $y_n(p)$  are: (a) single valued, (b) integrable, and (c)  $\lim_{p \rightarrow \infty} [p^c x_n(p)] = 0$  and  $\lim_{p \rightarrow \infty} [p^c y_n(p)] = 0$  for all  $c$ .

Equations for complex mixtures analogous to those for discrete mixtures for the enriching section are

$$x_n(p) = \frac{p y_n(p)}{\int_0^{\infty} p y_n(p) dp} \quad (4.3)$$

and

$$y_{n+1}(p) = \frac{R}{R+1} \frac{p y_n(p)}{\int_0^{\infty} p y_n(p) dp} + \frac{x_0(p)}{R+1} \quad (4.4)$$

where  $R$  and  $x_0(p)$ , the distribution function of the overhead product, have been specified *a priori*. The linearization of (4.4) follows in the same manner as previously. A function  $X_n(p)$  is defined such that

$$p y_n(p) = \frac{1}{R+1} \frac{x_0(p) X_n(p)}{\int_0^{\infty} x_0(p) X_{n-1}(p) dp} \quad (4.5)$$

where

$$X_{n+1}(p) = R p X_n(p) + p \int_0^{\infty} x_0(p) X_n(p) dp \quad (4.6)$$

or symbolically

$$X_{n+1}(p) = H X_n(p) \quad (4.7)$$

where  $H$  is a linear operator and

$$X_1(p) = p/R. \quad (4.8)$$

The iteration of (4.7) gives

$$X_n(p) = \frac{1}{R} H^{n-1} p \quad (4.9)$$

This form of the solution although not very useful here does settle the question concerning existence and uniqueness of the solution, for if (4.9) is written out in detail

$$X_n(p) = C_1(p) \int_0^{\infty} p^{n-1} x_0(p) dp + C_2(p) \int_0^{\infty} p^{n-2} x_0(p) dp + \dots + C_n(p) \int_0^{\infty} x_0(p) dp$$

where the  $C_k(p)$  are polynomials in  $p$  and the integrals are the successive moments of the overhead distribution function. Certainly for machine calculations these integrals are not difficult to compute. These integrals will exist from our previous hypothesis  $c$ .

However, an integral transform can be defined which will generate a solution which has some advantages. If  $f(i)$  is a function of  $i$  which is defined for integral  $i$ ,  $1 \leq i \leq m$ , then a finite transform  $T[f(i)] = \bar{f}(k)$  may be defined by

$$T[f(i)] = \bar{f}(k) = \sum_{i=1}^m \frac{f(i) x_0(i)}{\lambda_k - p(i)} \quad (4.10)$$

where  $x_0(i)$  is specified and  $\lambda_k$  is one of the roots of (3.7). Since the  $v_k(i)$  form a complete orthogonal set

$$f(i) = \sum_{k=1}^m Q_k v_k(i) \quad (4.11)$$

and hence

$$\bar{f}(k) = Q_k/C_k$$

where  $C_k$  is given by (3.11). The inversion formula for the finite transform introduced above is

$$f(i) = \sum_{k=1}^m \bar{f}(k) C_k v_k(i) \quad (4.12)$$

Moreover, the finite transform has the property

$$T[p(i)f(i)] = \lambda_k \bar{f}(k) - \sum f(i) x_0(i) \quad (4.13)$$

This could have been used to solve (3.4).

To return to the continuous case, suppose that  $x_0(p)$  is defined in the interval  $0 < p \leq a$ , where  $a$  is arbitrary, and, in general, large, and that  $x_0(p) = 0$ ,  $p > a$ . Let the interval  $(0, a)$  be divided into  $m$  equal parts, then (4.6) may be approximated by

$$X_{n+1}(p(i)) = R p(i) X_n(p(i)) + p(i) \sum_{j=1}^m x_0(p(j)) X_n(p(j)) \Delta p \quad (4.14)$$

where  $\Delta p = a/m$  and  $p(i) = i \Delta p$ . This however is but Eq. (3.4). It is desired to obtain the solution of (4.14) as  $m \rightarrow \infty$  and it is hoped that this will represent the solution of (4.6). To begin, a new function  $\rho(i) = \rho(p(i))$  is defined

$$\rho(i) \Delta p = \lambda_i - p(i) \quad (4.15)$$

where  $\lambda_i$  is that root of the characteristic equation (3.7) which satisfies the relation,  $p(i) < \lambda_i < p(i-1)$ . Therefore

$$0 < \rho(i) < 1, \quad 1 \leq i \leq m$$

and the characteristic equation becomes

$$\sum_{j=1}^m \frac{p(j) x_0(j)}{\rho(k) + k - j} = R \quad (4.16)$$

remembering that the mole fraction of the  $j$ th component is  $x_0(p(j)) \Delta p$ . If now  $\mu$  is a small but otherwise arbitrary number and if  $\epsilon \Delta p = \mu$ , then (4.16) can be transformed into

$$R = \sum_{j=1}^{k-\epsilon-1} \frac{p(j) x_0(j)}{\lambda_k - p(j)} \Delta p + \sum_{j=k+\epsilon+1}^m \frac{p(j) x_0(j)}{\lambda_k - p(j)} \Delta p + \overline{p(k) x_0(k)} \sum_{-\epsilon}^{\epsilon} \frac{1}{\rho(k) + j}$$

where  $\overline{p(k) x_0(k)}$  is some intermediate value of  $p(j) x_0(j)$  in the interval  $k - \epsilon \leq j \leq k + \epsilon$ . As  $m \rightarrow \infty$ , for any  $\lambda$ ,  $0 < \lambda < a$ , this reduces to

$$R = \int_0^{\lambda-\mu} \frac{p x_0(p)}{\lambda-p} dp + \int_{\lambda+\mu}^a \frac{p x_0(p)}{\lambda-p} dp + \lambda x_0(\lambda) \pi \cot \pi \rho(\lambda)$$

since

$$\lim_{\mu \rightarrow \infty} \sum_{-\mu}^{\mu} \frac{1}{\rho(\lambda) + j} = \pi \cot \pi \rho(\lambda)$$

If finally  $\mu$  is made arbitrarily small and  $a$  is very large, then formally

$$R = P \int_0^{\infty} \frac{p x_0(p)}{\lambda-p} d\lambda + \lambda x_0(\lambda) \pi \cot \pi \rho(\lambda) \quad (4.17)$$

provided that  $m$  is always chosen such that  $\mu m > 1$ , which is possible. The  $P$  associated with the improper integral denotes the Cauchy principal value of that integral. Equation (4.17) which can also be obtained rigorously by using residue theory then defines a new function  $\rho(\lambda)$ ,  $0 < \lambda < \infty$ , and such that  $0 < \rho(\lambda) < 1$ , which, in a sense, takes the place in the continuous problem of the eigenvalues in the discrete problem. We perceive from (4.15) that as  $m \rightarrow \infty$  the discrete spectrum of eigenvalues approaches a continuous spectrum and as a consequence it would be expected that the finite transform (4.10) would pass to an integral transform.

If it is supposed then that  $x_0(p)$  is a continuous, single valued, and integrable function and that it does not vanish on the  $p$ -axis, then the integral transform of a similarly restricted function  $f(p)$  may be defined as

$$T[f(p)] = \bar{f}(\lambda) = p \int_0^{\infty} \frac{f(p) x_0(p)}{\lambda-p} dp + \frac{f(\lambda)}{\lambda} w(\lambda) \quad (4.18)$$

where

$$w(\lambda) = R - P \int_0^{\infty} \frac{p x_0(p)}{\lambda-p} dp \quad (4.19)$$

One can readily show that

$$T[p f(p)] = \lambda \bar{f}(\lambda) - \int_0^{\infty} f(p) x_0(p) dp \quad (4.20)$$

which is the limiting form of (4.18). The inversion

formula may be formally derived by repeating the steps to obtain the characteristic equation, and thus

$$f(p) = T^{-1}[\bar{f}(\lambda)] = p P \int_0^{\infty} \frac{\bar{f}(\lambda) C(\lambda)}{\lambda-p} d\lambda + \frac{\bar{f}(p) C(p)}{x_0(p)} w(p) \quad (4.21)$$

To obtain an expression for the function  $C(\lambda)$  consider once more the finite problem. For the finite problem  $C_k$  was defined by (3.11)

$$C_k \sum \frac{p(i) x_0(i)}{[\lambda_k - p(i)]^2} = 1$$

On the other hand a comparison between (4.21) and (4.12) reveals that as the finite problem passes to the continuous problem, i.e.,  $\Delta\lambda \rightarrow 0$ , then  $C_k \simeq C(\lambda) \Delta\lambda$  where  $k\Delta\lambda = \lambda$ . However, as  $\Delta\lambda$  is made arbitrarily small

$$\sum \frac{p(i) x_0(i)}{[\lambda_k - p(i)]^2} \rightarrow \frac{\lambda x_0(\lambda)}{\Delta\lambda} \sum_{-\infty}^{\infty} \frac{1}{[\rho(\lambda) - j]^2} \quad (4.22)$$

where  $\rho(\lambda)$  is given by (4.15) and (4.17). But

$$\sum_{-\infty}^{\infty} \frac{1}{[\rho(\lambda) - j]^2} = \pi^2 \csc^2 \pi \rho(\lambda) \quad (4.23)$$

and therefore since  $\arctan x = \arcsin \frac{x}{\sqrt{1+x^2}}$

$$C(\lambda) = \frac{\lambda x_0(\lambda)}{[w(\lambda)]^2 + [\pi \lambda x_0(\lambda)]^2} \quad (4.24)$$

for all positive  $\lambda$ . Equation (4.24) may also be obtained by more refined methods [10].

Equation (4.6) may now be solved for, from (4.18),

$$T[X_n(p)] = \bar{X}_n(\lambda) = P \int_0^{\infty} \frac{X_n(p) x_0(p)}{\lambda-p} dp + \frac{X_n(\lambda) w(\lambda)}{\lambda} \quad (4.25)$$

it follows from (4.6), (4.20) and (4.18) that

$$\bar{X}_{n+1}(\lambda) = R\lambda \bar{X}_n(\lambda)$$

$$X_1(\lambda) = 1$$

Therefore

$$\bar{X}_n(\lambda) = (R\lambda)^{n-1}$$

and from (4.21) and (4.24)

$$X_n(p) = p P \int_0^\infty \frac{(R\lambda)^{n-1} C(\lambda)}{\lambda - p} d\lambda + \frac{(Rp)^{n-1} C(p)}{x_0(p)} w(p) \quad (4.26)$$

which is the solution of (4.6) and where  $C(p)$  is defined by (4.24). It may be shown that (4.26) satisfies (4.14).

Consider now the case where the function  $x_0(p)$  is continuous, single valued, and integrable, but vanishes only and everywhere in a set of intervals  $B$ ,  $b_k < p < a_k$ ,  $k = 1, 2, \dots, c$ , where  $a_k > a_{k+1}$  and  $b_k > b_{k+1}$ , and let the remaining part of the  $p$  axis be the region  $A$ . Then the characteristic equation is given by (4.17) for  $\lambda$  in  $A$  but in addition one can find  $c$  number  $\lambda_k$ ,  $\lambda_k$  in  $B$ , such that

$$\int_0^\infty \frac{p x_0(p)}{(\lambda_k - p)} dp = R, \quad 1 \leq k \leq c \quad (4.27)$$

where this integral is proper. Therefore, if

$$C_k \int_0^\infty \frac{p x_0(p)}{(\lambda_k - p)} dp = 1 \quad (4.28)$$

then the solution to (4.6) is

$$X_n(p) = p P \int_A \frac{(R\lambda)^{n-1} C(\lambda)}{\lambda - p} d\lambda + \frac{(Rp)^{n-1} C(p)}{x_0(p)} w(p) + p \sum_{k=1}^c \frac{(R\lambda_k)^{n-1} C_k}{\lambda_k - p} \quad (4.29)$$

where  $X_n(p)$  is defined only for  $p$  in  $A$ . Finally the limiting form of (3.13) is

$$x_n(p) = \frac{p x_0(p)}{R} + \frac{P \int_A \frac{\lambda^{n-1} C(\lambda)}{\lambda - p} d\lambda + \frac{p^{n-1} C(p)}{p x_0(p)} w(p) + \sum_{k=1}^c \frac{\lambda_k^{n-1} C_k}{\lambda_k - p}}{\int_A C(\lambda) \lambda^{n-1} d\lambda + \sum_{k=1}^c C_k \lambda_k^{n-1}} \quad (4.30)$$

for  $p$  in  $A$ .

2. *Semi-Continuous Mixtures.* Mixtures will

be called semi-continuous if in addition to containing an infinite number of components they contain a finite number  $m$  of components in finite concentrations. This is the most general mixture that can be considered. Let  $x_0(i)$  be the mole fraction of the  $i$ th distinguishable component which is present in finite amount. Then, following BOWMAN [6], the distribution function of the overhead product  $\bar{x}_0(p)$  may be defined as

$$\bar{x}_0(p) = x_0(p) + \sum_{i=1}^m \delta(p - p_i) x_0(i)$$

where  $\delta(p - p_i)$  is the Dirac delta function and  $x_0(p)$  is the distribution function of the continuous part of the mixture. Of course

$$\int_0^\infty \bar{x}_0(p) dp = \int_0^\infty x_0(p) dp + \sum_{i=1}^m x_0(i) = 1.$$

The case will be considered in which  $x_0(p)$  is continuous, single valued, and integrable along the whole  $p$  axis and it vanishes everywhere in a set of  $c$  intervals  $B$  as previously defined and is non-zero elsewhere, i.e. on the set  $A$ . Suppose also that  $p_i$ ,  $1 \leq i \leq m_1$ , is in  $A$  and  $p_i^+$ ,  $1 \leq i \leq m_2$  is in  $B$ , where  $m_1 + m_2 = m$ . Then

$$\bar{x}_0(p) \equiv x_0(p) + \sum_{i=1}^{m_1} \delta(p - p_i) x_0(i) + \sum_{i=1}^{m_2} \delta(p - p_i^+) x_0(i) \quad (4.31)$$

and the results of the previous section can be applied to the general problem. For, if

$$w(\lambda) \equiv R - P \int_0^\infty \frac{p \bar{x}_0(p)}{\lambda - p} dp \quad \text{for } \lambda \text{ in } A \quad (4.32)$$

$$C(\lambda) \equiv \frac{\lambda x_0(\lambda)}{[w(\lambda)]^2 + [\pi \lambda x_0(\lambda)]^2} \quad \text{for } \lambda \text{ in } A \quad (4.33)$$

$$\int_0^\infty \frac{p \bar{x}_0(p)}{\lambda_k - p} dp = R \quad \text{for } 1 \leq k \leq c + m_2 \text{ and } \lambda_k \text{ in } B \quad (4.34)$$

$$C_k \int_0^\infty \frac{p \bar{x}_0(p)}{(\lambda_k - p)^2} dp = 1 \quad \text{for } 1 \leq k \leq c + m_2 \text{ and } \lambda_k \text{ in } B \quad (4.35)$$

Then

$$x_n(p) = \frac{p \bar{x}_0(p)}{R}$$

$$\frac{P \int_A \frac{\lambda^{n-1} C(\lambda)}{\lambda - p} d\lambda + \frac{p^{n-1} C(p)}{p x_0(p)} w(p) + \sum_{k=1}^{c+m_1} \frac{\lambda_k^{n-1} C_k}{\lambda_k - p}}{\int_A \lambda^{n-1} C(\lambda) d\lambda + \sum_{k=1}^{c+m_1} \lambda_k^{n-1} C_k} \quad (4.36)$$

for  $p$  in  $A$  and

$$x_n(p) = \frac{p \bar{x}_0(p)}{R} \frac{\int_A \frac{\lambda^{n-1} C(\lambda)}{\lambda - p} d\lambda + \sum_{k=1}^{c+m_1} \frac{\lambda_k^{n-1} C_k}{\lambda_k - p}}{\int_A \lambda^{n-1} C(\lambda) d\lambda + \sum_{k=1}^{c+m_1} \lambda_k^{n-1} C_k} \quad (4.36a)$$

for  $p = p_i^+$ ,  $1 \leq i \leq m_2$ . Moreover from (4.32), (4.33), and (4.36) for  $p = p_i$ ,  $1 \leq i \leq m_1$

$$x_n(p) = \frac{p \bar{x}_0(p)}{R} \frac{P \int_A \frac{\lambda^{n-1} C(\lambda)}{\lambda - p} d\lambda + \sum_{k=1}^{c+m_1} \frac{\lambda_k^{n-1} C_k}{\lambda_k - p}}{\int_A \lambda^{n-1} C(\lambda) d\lambda + \sum_{k=1}^{c+m_1} \lambda_k^{n-1} C_k} \quad (4.36)$$

Similar results may be obtained for the stripping column and useful asymptotic expressions, analogous to (3.26), may be derived.

#### NOTATION

- $C_k$  = function defined by Eq. (3.11)  
 $C(\lambda)$  = function defined by Eq. (4.24)  
 $D$  = moles of overhead product per mole of feed  
 $i, j$  = component designating variable discrete case  
 $L$  = moles of liquid from  $n$ th plate  
 $n$  = plate designating variable  
 $p(i)$  = reciprocal relative volatility for  $i$ th component in rectification section  
 $R$  = reflux ratio in rectification section  
 $v_k(i)$  =  $k$ th eigenfunction - defined by Eq. (3.8)  
 $w(p)$  = function defined by Eq. (4.19)  
 $W$  = moles of residue from column bottom  
 $x_n(i)$  = mole fraction of  $i$ th component in liquid on  $n$ th plate  
 $x_n(p)$  = distribution function of liquid on  $n$ th plate  
 $x_0(i), x_0(p)$  = composition of total condensate and reflux  
 $X_n$  = function defined by Eqs. (3.2) and (4.6)  
 $y_n(i)$  = mole fraction of  $i$ th component in vapour from  $n$ th plate  
 $y_n(p)$  = distribution function of vapour from  $n$ th plate  
 $\alpha(i)$  = relative volatility  
 $\lambda_k$  = root of Eq. (3.7)  
 $\rho(p)$  = function defined by Eq. (4.15)

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## An analysis of the principles of batch and continuous operation

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**Summary**—An analysis is presented of the meaning of the words "batch" and "continuous," mainly with regard to transfer processes (also called diffusional processes) and with an extension for chemical reactors. In this analysis the various principles of operating such processes are examined. It emerges from this analysis, that there is much diversity in the literature with regard to the use of such words as batch, intermittent, continuous, step wise, co-current, cross-flow, multiple contact and so on. Proposals are made for a handling of such terms, that is believed to be a systematic one.

Finally an effort is made to tie the various arguments that enter into a comparison between batch and continuous processing to various aspects recognised in the above analysis.

**Résumé**—L'auteur précise la signification qu'il donne aux termes "batch" et "continuous," surtout en ce qui concerne les processus de transfert (appelés aussi processus de diffusion) et par extension dans le cas de réacteurs chimiques. Dans cette analyse, il examine les divers principes d'utilisation de tels processus. Il ressort de cette analyse qu'il y a dans la littérature une grande diversité dans l'emploi de mots tels que "batch," "intermittent," "continuous," "step wise," "co-current," "cross-flow," "multiple contact," et ainsi de suite. L'auteur fait des propositions pour l'emploi systématique de ces termes. Finalement, il fait un effort pour réunir les divers arguments qui entrent dans la comparaison entre "batch" et "continuous" en tenant compte des divers aspects mis en évidence dans l'analyse ci-dessus.

### INTRODUCTION

The chemical engineer is confronted with the choice between "batch operation" and "continuous operation" in all or nearly all of his physical and chemical processes.

The ideal should be to lay down hard and fast rules by the application of which for any specific case an unambiguous conclusion can be obtained. It has become apparent that such a goal cannot be reached, and that the best one can do is to enumerate a number of factors or arguments which may arise and should be considered.

These various arguments have been collected, for which reference is made to the 11 articles or short statements on continuous processing, published in *Chem. Met. Eng.* in 1945 [2].

Recently a symposium was held in the Netherlands by the Royal Institution of Engineers where, after a general introduction by VERSCHOOR, some speakers gave their views on continuization in their industries, viz. ASSELBERGS (beet sugar), GERRITSEN (salt, caustic and chlorine) and LEVISON (viscose rayon), and where KRAMERS

presented a review on holding times. The proceedings have just appeared in *Chemisch Weekblad* 1954 50 145.

Some of the arguments raised can be translated in terms of money, but not all. The choice is therefore not a matter of economy only, but it also depends on experience and good judgment.

It is proposed to discuss here, *why* the problem of opposing "batch" to "continuous" is so complex. A very important cause of this complexity is the fact that the notions "batch" and "continuous" both are found to be very vague and ill-defined. They are used in the literature with various meanings attached to them. Literally, the words "batch" and "continuous" do not have opposite meaning, so that it might be asked whether they are mutually exclusive and together cover all possibilities.

Another disconcerting feature is the fact that there are often many gradations between the most discontinuous and the most continuous version of a process. For instance, if two materials are contacted, one may be flowing and the other at

rest. Also, pulsating flow is less "continuous" than steady flow.

A process, which is continuous at first sight, will turn out to have a batch aspect if there is a product which accumulates, such as :

- scale in boilers,
- carbon on catalysts,
- volatile hydrocarbons in circulating volatile solvent in mineral oil extraction plants,
- impurities in circulating non-volatile solvents, in extraction plants where the products are distilled off from the solvent,
- raags at the interface of a continuous settler,
- over-polymerized product in polymerization units.

An indication of the above difficulties is also found in the fact that the expressions "semi-continuous" and "semi-batch" are sometimes used. Thus, HUNTER and NASH [4] describe extraction in a counter-current system of mixers and settlers as a "semi-continuous process" as opposed to the "continuous" process in an extraction tower.

WALKER, LEWIS, McADAMS and GILLILAND [17], page 506, use "semi-batch" with reference to a percolator, where a gas flows through a bed of adsorbent. Obviously "semi-continuous" is quite different from "semi-batch."

These arguments are considered sufficient to prove that an analysis of the possible meanings of the words "batch" and "continuous" and an analysis of possible alternative expressions such as "intermittent" (see, e.g. WALKER, LEWIS, McADAMS and GILLILAND's intermittent distillation [17], page 551-552, and intermittent drying [17], page 622) are prerequisites to the discussion of the choice between "batch" and "continuous" treatment.

Further to illustrate the necessity of careful analysis one may quote one of the authors in the 1945 *Chem. Met. Eng.* reports [2], who traced the failure of a continuous process to the labourer, who was supposed to fill a salt bin, being fast asleep. This continuous process failed on a discontinuous aspect.

The afore-mentioned choice has to be made in all branches of engineering. For the present treatise some limitation, however, is considered desirable. An analysis will therefore be made for the important group of unit operations describable as "transfer processes" or "diffusional processes," the group including distillation, heat transfer, extraction, etc. The results will be applied to the equally important group of chemical reactors.

Finally, an effort is made to tie some of the usual arguments pro and contra "batch" and "continuous" to the results of these analyses.

This analysis is founded upon unpublished work by W. J. D. VAN DIJCK and the author in 1935 when a nomenclature was developed to be used in describing transfer processes. Use thereof was made by A. W. J. MAYER in 1937 [4].

#### INTRODUCTION TO A DISCUSSION OF THE PRINCIPLES OF BATCH AND CONTINUOUS OPERATION AS APPLIED IN TRANSFER PROCESSES

The analysis reveals that the word "continuous" is used in three different ways, sometimes opposed to "in stages," sometimes with "batch" as its counterpart.

One form is continuity with respect to place, the two others are continuity with respect to time.

These various possibilities are most fully developed in countercurrent processes. These are therefore to be examined first and to be followed by other processes in the following order :

- Countercurrent processes,
- Single-stage processes,
- Percolator processes,
- Cross-flow processes.

It should, however, be mentioned that this list only covers the simpler possibilities. For instance, if percolators are used in series in cyclic rotation the action becomes substantially continuous and in countercurrent ([17], page 506). Also, bubble plate columns show countercurrent between and cross-flow on the trays.

# ANALYSIS OF COUNTERCURRENT PROCESSES

## 1. Continuity with respect to place

Upon examination of the compositions\* in a countercurrent transfer system it is seen, that their variation with place is either gradual (in packed columns) or stepwise (in plate columns, in systems of mixers and settlers).

It is proposed to denote such processes by the names of "gradual"\*\*\* and "stagewise" processes, respectively.

The difference between these groups of processes has a profound influence on the mathematics of calculating their performance.

Gradual processes are described by differential equations with place as a (continuous) variable. Processes in stages are described by finite difference equations which, in fact, are simple algebraic equations. In the latter, place is a discontinuous variable which assumes only whole number values (i.e., stage numbers).

The results, however, obtainable by the two processes are very much the same. Any two-component separation is obtainable by both. The theoretical argument that more-component separations cannot be matched because of differing rates of transfer for different components seems to be of academic interest only. The difference "gradual" versus "stages" is therefore from the practical point of view one of mode of operation rather than one of principle.

The literature reveals that :

- there are cases where the word "batch" has been used to describe a stage-wise or even a one-stage operation, and
- gradual countercurrent processes have thus far been normally described as continuous or differential countercurrent processes.

*Use of "batch"*—SHERWOOD and PIGFORD [12], page 392, mention "the single contact in which

\* The temperature in heat transfer will be omitted in the following for the sake of simplicity.

\*\*\* Unfortunately, the Latin "gradus" means step. However, the development of the meaning of the word "gradual," originally "step by step" has been via "by a great number of very small steps" toward its present meaning of a change without steps.

the solvent and solution are brought together for a single batch extraction." In the accompanying figure this is shown to be carried out in a mixer and settler with a continuous feed. The essential feature clearly is the single contact, i.e. the single stage and the fact, whether the treatment is continuous or not, is of secondary importance for the discussion.

MANLEY *et al.* [7] mention "batch or step counterflow extractions, consisting of passing oil and solvent in counterflow through a number of separate mixers and settlers."

STRATFORD *et al.* [13] mention that "a batch method or countercurrent treatment" are alternatives to be used in extraction. They make "batch" the equivalent of "single stage."

WALKER, LEWIS, McADAMS and GILLILAND [17] page 465-466, and Fig. 161, compare "countercurrent flow" to "batch operation."

*Use of "continuous countercurrent"*—TREYBAL [15], page 125, puts "continuous contact" opposite to "stage-wise contact."

MANLEY *et al.* [7] mention "continuous counterflow extraction in a single apparatus."

SHERWOOD and PIGFORD [12], page 394, oppose "continuous countercurrent" to "multiple contact countercurrent."

The conflicts in the nomenclature in this field are clearly brought out by quoting in contrast thereto BROWN [1], page 301, who says : "countercurrent multiple contact may be either batch or continuous." Here, continuous stands for non-intermittent (see page 42).

*Use of "differential countercurrent"*—"Continuous countercurrent differential contact," according to PERRY [10], page 717 = continuous gradual countercurrent. In the next paragraph the adjective "true" is used to distinguish this process from multi-stage countercurrent.

## 2. Continuity with respect to time

A convenient starting point is the rather obvious statement, to be further refined and modified in the following, that "batch" refers to the feed being introduced in separate charges and "continuous" to the fact that the process variables (flows, compositions, temperature) are time-independent (see [2], pages 101 and 118).

Examples are the well-known processes of batch and continuous rectification, each of which can be carried out gradually (in a packed column) or stage-wise (in a plate column).

For stage-wise processes, not involving a vapour or gas a further choice of alternatives becomes apparent. Stage-wise countercurrent extraction, for instance, may be carried out in two ways:

1. In separatory funnels and in similar large-scale equipment. Here, the same equipment serves in regular rotation for all functions (mixing, settling, transport).
2. In mixers and settlers with pumps, where the units of equipment do not change their function.

The first of these alternatives falls under the description of "batch" as given above. If, however, one regards batch distillation as a typical batch process, it is seen that the extraction in separatory funnels may be lacking the characteristic features of a typical batch process, such as the gradually changing compositions and the possibility to collect a great many different fractions. In fact, the countercurrent extraction in separatory funnels is frequently used to simulate the continuous operation of the other alternative, mixers and settlers, the latter being more difficult to realize on a small scale.

If the stages in both are ideal, extraction conditions are the same, and the extractions are continued beyond the initial transient period, the products of both extractions are identical.

Notwithstanding the close similarity to a continuous process as described above, the extraction in separatory funnels is not continuous in the sense that the state at a given point does not vary with time.

Obviously the definitions of batch and continuous must be amended to make possible a "continuous countercurrent extraction in separatory funnels." This can be done by using different expressions for the continuity of the stage and for the continuity of the process as a whole.

In the following the process using separatory funnels will be called "intermittent" and the process using mixers and settlers "non-intermittent." The essential feature to distinguish

batch and continuous will be the fact whether the products of the process are changing or constant. In this manner the process in separatory funnels – after its transient period – will be a continuous countercurrent process in intermittent stages.

Attention is drawn to the fact that the expressions "intermittent" and "batch" are both used by WALKER, LEWIS, McADAMS and GILLILAND [17].

In the present treatise usually the names are just reversed, as is seen from the following survey:

W., L., McA., G.		Author
p. 551	intermittent	batch distillation
	distillation	
p. 622	intermittent drying	batch drying
p. 517	batch distillation	cross-flow batch
		distillation
p. 509	ideal single-stage	intermittent single
	batch adsorption	stage adsorption

Our present choice may be justified as follows:

In the intermittent extraction in separatory funnels it is essential that each funnel is used a great many times in the same process, i.e. with intermissions. In the processes commonly called "batch distillation," "batch drying," etc., the method consists of the working up of a single charge. This need not be ever repeated and certainly need not be linked up with its independent repetitions, as the expressions "intermittent distillation" and "intermittent drying" would suggest.

For the simple gradual processes as discussed here the distinction intermittent/non-intermittent does not arise. There is only batch and continuous gradual countercurrent.

The definitions for continuity do not apply to the approach to the steady state of a countercurrent process. This approach is itself a batch process (transient from empty to full as contrasted to transient from full to empty in other batch processes). It is of course not the intention to let the transient interfere with the definition of continuous processes.

#### Observations on nomenclature in literature

1. For transient + continuous intermittent countercurrent treatments the name "pseudo-



countercurrent" is sometimes used (HUNTER and NASH [5], page 839).

The "pseudo" would seem superfluous. A certain amount of interpretation to recognize countercurrent is always necessary, even in a plate fractionation column where descending liquid and ascending vapour move through different regions of space.

2. A batch intermittent countercurrent treatment with a single introduction of feed is described by the same authors as multiple fractional distribution.
3. "Batch countercurrent multi-stage extraction" (PERRY [10], page 718) = continuous intermittent countercurrent extraction, i.e. "batch" serves to indicate the intermittent operation of the stages.
4. "Countercurrent multiple contact extraction" (= countercurrent extraction in stages) can according to SHERWOOD and PIGFORD [12], page 394, be carried out in batch or continuous, exemplified by systems of mixers and settlers, as used in batch operation, on the one hand, or by the perforated plate column on the other.

These authors add: "At first glance the latter would appear to be an example of continuous countercurrent flow but in reality should be classified as continuous multiple contact, since each plate acts as a combined mixer and settler."

In our classification the operation of the mixers and settlers and the perforated plate column would fall under the same heading (i.e. countercurrent in non-intermittent stages).

#### ANALYSIS OF SINGLE-STAGE PROCESS

For the single stage, consideration of the three classification principles as developed for countercurrent shows:

- |                                   |   |
|-----------------------------------|---|
| 1. gradual/stages                 | the process is already limited to one stage   |
| 2. non-intermittent/-intermittent | } become identical for a process in one stage |
| 3. continuous/batch               |   |

There are therefore two modes of execution of

a single-stage process (for extraction: mixer + settler, and separatory funnel).

The names non-intermittent and intermittent will be given preference because the discontinuous process has *not* the property to make products of varying composition. However, continuous and batch are in common use.

Unfortunately, "batch" is often used to describe laboratory extractions where the characteristic feature is "single stage." Authors will say that they compare (laboratory) batch extractions with (plant) countercurrent extraction.

#### Observations on nomenclature in literature

Single contact is an acceptable equivalent to single stage.

"Batch treatment" (see STRATFORD *et al.*, as cited on page 41) is unnecessarily limited. "Single-stage batch treatment" is acceptable if it is wanted to convey the intention that "continuous" i.e. non-intermittent operation is not included.

"Simple distillation" by a "single vaporization used to separate partially two or more volatile liquids" (WALKER *et al.* [17], page 516, see also [11], page 107) is a term meant to cover both single-stage distillation ("continuous simple distillation," such as flashing) and gradual cross-stream distillation ("batch" or "differential" distillation), the latter to be discussed later.

This might convey the impression that these processes are the continuous and discontinuous version of the same, which, of course they are not.

Discontinuous (i.e. intermittent) single-stage distillation is, however, conceivable but it is rather impractical because of the large volume of a vapour. Its analogue in extraction (the separatory funnel) is, however, very common.

#### ANALYSIS OF PERCOLATION PROCESSES

In percolators as used in chromatography and related processes each phase is contacted successively with portions of the other, as in countercurrent, but only one of the phases is moving and the other is stationary. For this reason the percolation in a fixed bed is of necessity a batch process.

THIELE [14] used the name "percolation" for



processes where a fluid (gas or liquid) is passed through a bed of a granular solid. He had in mind fixed beds only and there is indeed a need for a term describing such operations. WALKER *et al.* ([17], page 465) also refer to percolation filters being fixed beds.

Percolation as defined by THIELE is a gradual process, but the principle may be extended to cover stage-wise processes and these may be carried out in non-intermittent and intermittent manner. Thus CRAIG's well-known extraction process [20] is stage-wise and intermittent, and the passage of a gaseous mixture through a series of washing bottles filled with an absorbent liquid is a stage-wise and non-intermittent percolation process.

#### ANALYSIS OF CROSS-FLOW

##### (-STREAM OR -CURRENT) PROCESSES

The cross-flow principle is easiest recognized, when the phase to be treated, say by extraction, is flowing continuously through a number of mixers and settlers, in each pair of which it is meeting a fresh stream of the other phase. This cross-flow process is described as stage-wise, non-intermittent and continuous. By replacing each mixer + settler by a separatory funnel the stage-wise, intermittent continuous version is obtained. There is also a gradual cross-stream process, where the phase to be treated is, on its way, differentially extracted, vaporized or the like.

Upon comparing countercurrent and percolation, it is seen that the relative movement of the phases was the same, whilst the movement with regard to the vessel determined whether the process could be a continuous process (both moving) or had to be a batch process (one at standstill).

These same possibilities exist here :

In cross-flow as described above, the phase to be treated moved from one mixer-settler combination or one separatory funnel to the next, and the process was necessarily continuous. There is, however, no necessity to move the phase to a new vessel before continuing the treatment.

By leaving this phase in the same vessel the corresponding batch processes are obtained. However, all products being the same in the batch and

continuous version, it is practical to employ the name cross-flow for both. The treatment may be simultaneously at different places or successively at the same place, i.e. place in one case is equivalent to time in the other. Gradual cross-flow may therefore be continuous in place or in time.

Thus an ASTM distillation – when neglecting some slight rectification effect – will be termed a gradual cross-flow process and the so-called multiple-batch extraction is cross-stream in stages. For such gradual cross-flow to occur it is not necessarily required that one phase is removed from the treating vessel.

In those batch crystallization processes, where mixed crystals are formed, the once formed crystals are withdrawn from further reaction with the liquid by newly deposited layers of solid. The continuous crystallizer on the other hand operates in one stage and produces a homogeneous product.

#### *Observations on nomenclature of cross-flow processes in literature*

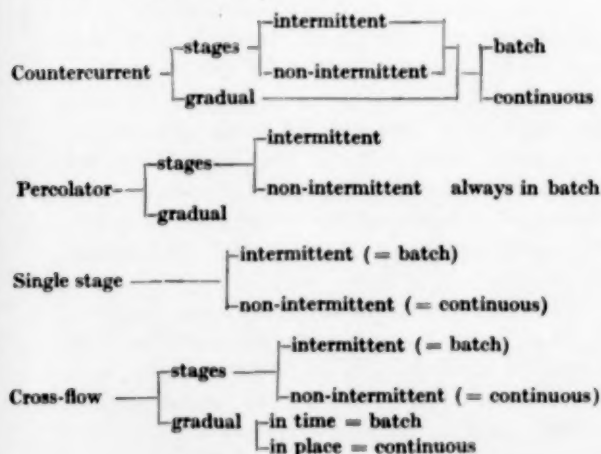
1. The name "co-current" for cross-flow is considered ill-chosen ([15], page 129 and 146; [4], page 340; [6], page 352; [16].)
2. "Simple multi-stage contact" ([10], page 716), and "simple multiple contact" ([1], page 301) are cross-flow in stages.
3. "Multiple batch extraction" is also cross-flow in stages.
4. The gradual, cross-flow batch distillation is often referred to as differential distillation (see [17], page 532), its extraction analogue as differential extraction (see [15], page 129).
5. WALKER *et al.* ([17], page 517), use the expression differential distillation, as discussed on page 43.
6. CRAIG and CRAIG [20], page 246, describe laboratory extractors for the extraction of a batch of liquid with a solvent which is continuously being recovered by distillation (as in the Soxhlet apparatus). Such extraction would be a gradual cross-flow batch extraction in our nomenclature. It is classed as "continuous single stage." Apparently

"continuous stands for 'gradual,' the "single stage" refers to the single vessel, even if this is used for a gradual process.

7. SHERWOOD and PIGFORD describe: "Multiple-contact extraction, using fresh solvent in each contact" ([12], page 392-3). The name is clear (= our cross-flow in stages, operated continuously).
8. The use of "multiple-contact," without any further restriction to describe stagewise cross-flow (see [5], page 837) is open to criticism. Multiple-contact in fact also occurs in stagewise countercurrent equipment. Thus, TREYBAL (see [15], pages 129, 146 and 156) rightly distinguishes "co-current (our crossflow) multiple contact" and "countercurrent multiple contact." His statement (page 129) that countercurrent multiple contact is necessarily "continuous" but may be simulated "in batch" obviously refers to non-intermittent and intermittent treatment, whereas the extraction analogue of batch distillation in a plate column has not been considered.\*

The following table gives a survey of the classification principles discussed so far.

#### Subdivision of transfer processes



\* Note added in proof:

Batch extraction in plate columns has been discussed by PRATT, H. R. C.; *Chem. Eng. Sci.* 1954 3 189.

Further criteria of subdivision not to be discussed here deal with interchanging the phases and choosing the place of the feed, so that principles such as rectifying, stripping and complete rectification, and the analogous concepts for cross-flow can be introduced.

#### APPLICATION TO CHEMICAL REACTIONS

A first effort has been made to have some of the ideas developed for diffusional processes applied to chemical reactions. There is a number of chemical reactions between two phases which proceed towards an equilibrium just as most diffusional processes, and in these cases the systematic subdivision can be the same as for diffusional operations.

Here countercurrent and percolation are encountered as important modes of operation. Examples are:

- absorption of  $H_2S$  and  $CO_2$  in weakly alkaline solvents such as  $K_3PO_4$  solution;
- extraction of weak acids such as mercaptans from gasolines with ordinary or solutized caustic solutions;
- simultaneous esterification and distillation;
- various ion exchange processes.

By analogy with diffusional processes the above-mentioned countercurrent or percolation need not be employed if the degree of reaction in a single stage is good enough.

Another important group is found in the homogeneous reactions. These may be carried out in a single stage (one stirred tank), in more stages (series of stirred tanks) or gradually (turbulent flow in tube).

In the single-stage process, by analogy with transfer processes, the concepts of intermittent/non-intermittent and batch/continuous should merge. With the transfer processes the names intermittent/non-intermittent were preferred, since the two forms can yield the same products and do so when the stage is ideal. The occasion to compare equipment sized for intermittent and non-intermittent operation did not arise in transfer processes, because the necessity to contact, exchange and separate causes the

intermittent equipment to be different in type from the non-intermittent.

In homogeneous chemical reactors, the same type of stirred reactor may serve for both. Here, the reaction rate, which may be very slow, is solely determining the size. In that case the choice of batch versus continuous operation becomes of prime importance for the reactor size, or inversely, for given size, for the fraction reacted.

A considerable amount of work has been done on the comparison of continuous and batch reactors, see, for example, PIRET and co-workers [3, 8] and WEBER [19] covering single, successive and simultaneous reactions, both reversible and irreversible, of various orders.

In the single reaction one is interested in the fraction converted only. Here, in the continuous reactor all reaction takes place at the final concentrations of the reactants, hence slower than in the batch reactor (except for zero-order reactions). Consequently the continuous reactor has the lower conversion for equal volume or the larger volume for equal conversion. The difference is most strongly felt for higher-order reactions and for high percentages of conversion. This disadvantage of continuous reactors can be offset to a certain extent by using more than one reactor in series, when the earlier vessels in the series have the advantage of a higher reactant concentration.

If there are consecutive and simultaneous reactions the yields of desired product calculated on converted feed material may also differ. MACMULLIN [2] has examined this effect for chlorination of benzene. He found that the yield of monochloro benzene is higher in batch chlorination.

Another argument is met in copolymerization.

Due to the fact that the different monomers have in general different reaction rates, in batch copolymerization polymers are formed of changing composition. In continuous copolymerization the polymer, being formed in a medium of constant composition, is uniform as regards chemical nature. These predictions have been verified by WALL, DELBECQ and FLORIN [8].

This state of affairs is analogous to the one discussed for crystallization (page 44).

#### TECHNICAL ARGUMENTS PRO AND CONTRA BATCH AND CONTINUOUS

In discussing batch versus continuous obviously all cases where "batch" has been used in the sense of "stage" and "continuous" in the sense of "gradual" should be disregarded, however interesting the comparison of "stage" versus "gradual" in itself may be.

Our comparison is to be related to continuity in the time. For stage-wise diffusional processes in addition to batch/continuous, as related to the process as a whole, the principles of intermittent/-non-intermittent, as related to the single stage, were distinguished. For chemical reactors such a further distinction need not usually be made.

In continuous non-intermittent and in continuous gradual processes each place in the equipment has its well defined function. However, there must be equipment for each aspect of the whole process. Thus, a continuous distillation process to separate  $n$  components requires  $n-1$  columns.

In a continuous intermittent process several dissimilar functions are combined in each contactor (e.g. mixing and settling).

In a batch process similar functions under different conditions are also combined in one unit (e.g. separating component 1 from the mixture of components 2... $n$ , separating component 2 from the mixture of components 3... $n$ , and so on, in a batch distillation).

Consequently, the batch process needs less equipment than the continuous process.

The batch process therefore being less costly to install, it is favoured for small units, where equipment costs count relatively heavily, and for new processes, where pay-out is uncertain. This difference is more important the more functions the batch equipment has, e.g. with distillations to produce a great many fractions.

The continuous process, being more complex, is more difficult to control manually so that control is more likely to be fully automatic, with a consequent further increase of capital cost.

The usual comparison therefore is:

continuous :	fully automatic control, little labour
batch :	less control equipment, labour required for maintaining the sequence of operations.

If, however, the batch process is to be fully automatic as well, its control may well become more complicated than the control of the continuous unit.

The batch process on account of its flexibility is favoured for new and unknown processes and for feeds variable in nature, composition and amounts.

These arguments count very heavily if the process serves an analytical purpose only (e.g. analytical rectification, chromatography).

In installing a "continuous" process the hidden batch aspects due to accumulating reaction products, as discussed earlier must be considered. Although some types of accumulation may reach a steady value, the efficiency of the process may have been impaired by that time to such an extent, that the arguments even then count in choosing between batch and continuous processing.

Batches of gas are usually avoided because of the low density of gases.

The explosion motor is a notable exception and there are some rare cases where chemicals might

be produced by executing a fast reaction many times a second in the same container.

Heat economy by heat exchange is most easily obtained in continuous processes, where all flows are continuous and the temperatures constant. The use of multiple effect certainly requires continuity.

In discussing such chemical reactors, where the rate of reaction was a determining factor for the size, the continuous reactor had to be larger than the batch reactor. The real difference is smaller than the theoretical one, because the batch equipment needs off-time for filling and emptying.

In chemical reactions where the product is an intermediate in a sequence of consecutive reactions the choice between batch and continuous will influence the ratio of yields of desired and by-products.

It is clear from the above that the choice between batch and continuous operation may well be such, that the first small unit for a new process is advantageously installed in batch and the subsequently erected larger unit is a continuous one.

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## Book review

**Ullmanns Enzyklopädie der technischen Chemie**, 3rd edition, by Dr. WILHELM FOERST.

Vol. 3. **Abietinsäure bis Arsenverbindungen**, XI + 851 pp, figs., tabs., 19 × 27 cm, bound. DM 108.—.

Vol. 4. **Arzneimittel bis Calcium**, XI + 842 pp, figs., tabs., 19 × 27 cm, bound. DM 108.—.

Published by Urban & Schwarzenberg, München - Berlin, 1953.

In the third edition of Ullmanns encyclopedia, volumes 3 and 4 are the first alphabetical ones to be published. Volume I, "Chemischer Apparatebau und Verfahrenstechnik," was published in 1951 as a preliminary to the alphabetical series and treated of such matters as unit operations, chemical reactors and thermodynamics. Volume 2, due this year, will be entitled "Betrieb und Laboratorium."

It was the original intention of the publishers to finish two volumes each year. Until now, the rate of appearance has been one volume per year. Although it is normal practice to publish the parts of an encyclopedia at intervals, the disadvantages inherent in this system seem to be particularly noticeable in this work. The reasons for this can be found in the rapid growth of chemical industry, and in the fact that there is so much detail in these books. It is to be hoped that the publishers will overcome this difficulty as soon as possible.

A comparison with the 2nd edition shows in the first place a decrease in the number of main headings. There is a tendency to group related subjects under one heading and this tendency is stronger than it was in the second edition. Correspondingly, there is an increased number of "see" - references. The editor has thus achieved improved readability of this text.

Moreover the subject matter has been conveniently arranged without either keeping too strictly to alpha-

betical order or presenting to the public a collection of monographs. In spite of this, much is still to be said in favour of the preparation of interim-indexes, especially since modern methods of editing and reproduction have greatly reduced their cost.

The type of information given under the various headings is the same as in the former edition: physical, chemical and physiological properties, preparation and manufacture, analysis, applications, economics, etc. Extensive application of flow-sheets and sketches of apparatus used in industry greatly contributes towards giving a clear presentation of modern manufacturing processes. The tremendous growth of chemical industry in the past twenty years clearly shows in such chapters as "Azetylen," "Ammoniak, synthetisches," and "Butylalkohole." Literature references among which those to patents rank first, are numerous throughout both volumes. The greater part of all references is given in the text rather than at the ends of sections. In the opinion of the reviewer, footnotes instead of scattered references would improve the readability.

A comparison of Ullmanns work with Kirk and Othmer's Encyclopedia of chemical technology, reveals in the first place a difference in the approach to the subject matter. The American work is more narrative in character than its German counterpart, in which the individual references used in compiling the text stand out more clearly. Also, in Kirk-Othmer less attention is paid to foreign processes than in Ullmann. Volumes 3 and 4 of the latter work contain much more technical information (estimated at 30%) and less pure chemistry than the corresponding American volumes.

For most cases preference will certainly be given to Ullmann. To all who are interested in chemical technology this work is heartily recommended.

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VOL.  
4  
1955